The Physicochemical Properties of Secondary Organic Materials

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The Physicochemical Properties of Secondary Organic Materials

A dissertation presented

by

Yue Zhang

to

The School of Engineering and Applied Sciences

in partial fulfillment of the requirements

for the degree of

Doctor of Philosophy

in the subject of

Engineering Sciences

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The Physicochemical Properties of Secondary Organic Materials

Abstract

The physicochemical properties of the secondary organic materials (SOMs) that constitute the particle phase have potentially important consequences for the growth, the reactivity, and ultimate fate of atmospheric organic aerosols, thereby affect climate, human health and visibility. A quantitative analysis of the physicochemical properties of the SOMs is important, but challenging. This thesis presents laboratory studies of α-pinene derived SOMs, which is one of the major components of secondary organic aerosols (SOAs) in the forests, by combing a flow tube reactor, aerosol particle mass analyzer (APM) and other online/offline measurement techniques.

A water-jacketed constant temperature flow tube reactor was built to produce SOM particles grown from either condensation or coagulation. Different ratios of α-pinene enantiomers were mixed and injected into the flow tube reactor for dark ozonolysis. A matrix of organic precursor and ozone concentrations was designed and tested in order to determine the optimal concentration to switch between condensation and coagulation. Results show that at 51 ± 1 ppm O₃, condensation is the dominant growth mechanism when the α-pinene concentration is 0.125 ± 0.001 ppm, and coagulation is the dominant growth mechanism when the α-pinene concentration increases to 1.00 ± 0.03 ppm. A combination of both growth mechanisms is observed when the α-pinene concentration is in between the described values.
The study also proposed and tested the hypothesis that a 50:50 mixture of α-pinene enantiomers may result in SOM particles that have different physical properties, such as number-diameter distributions, when compared with those particles generated from a single enantiomer of α-pinene. The experiment was conducted within the condensational growth regime so that the chirality induced structure differences in oligomers can be maximized during the nucleation and condensation. Nevertheless, our analysis indicates that, after removing the effects of ozone and temperature, the chirality-induced effects are minimal and within our detection limit. Even though the results were negative, the method used in this experiment provided useful experience for the viscosity related experiments in this thesis.

Another important property of the SOM is its viscosity. The viscosities of atmospheric particles determine whether their interactions with surrounding gases are confined to the surface or can proceed to the interior. Viscosities affect the gas-particle diffusion rate, and ultimately influences the SOM’s other physical properties, such as particle size, and chemical properties, such as reactivity. The work presented in this thesis estimates the viscosity of submicron organic particles while they are still suspended as an aerosol without further post-processing techniques that can have the possibility of altering the properties of semivolatile materials. The results show that the studied particles are semisolid up to 58% relative humidity (RH) and may become liquid only at a higher RH. These results imply that atmospheric particles, at least those similar to the ones studied and for low to middle RH regimes, are expected to reach equilibrium only rather slowly with the chemical composition of the gas phase, sometimes on timescales longer than the actual residence time of the particles in the atmosphere.
Last but not the least, the results of offline particle analysis from two collaboration studies are also discussed in this thesis. The results show how water vapor, or RH, affects the physicochemical properties of the α-pinene derived SOM particles. The results show how water vapor, or RH, affects the physicochemical properties of the α-pinene derived SOM particles. In one study, the diffusivity is underestimated by approximately 8 orders of magnitude if calculated from the Stokes-Einstein equation, which suggests the breakdown of Stokes-Einstein equation for small gas molecules. The second study shows the surface properties of SOM particles can be influenced by the RH, leading to a difference of the gas-particle interactions at the particle surface.
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Previously Published Work

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### Abbreviations

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<tr>
<td>VOC</td>
<td>Volatile organic compound</td>
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<tr>
<td>BVOC</td>
<td>Biogenic volatile organic compound</td>
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<tr>
<td>SOA</td>
<td>Secondary organic aerosol</td>
</tr>
<tr>
<td>SOM</td>
<td>Secondary organic material</td>
</tr>
<tr>
<td>RH</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>VBS</td>
<td>Volatility basis set</td>
</tr>
<tr>
<td>APM</td>
<td>Aerosol particle mass (analyzer)</td>
</tr>
<tr>
<td>CCN</td>
<td>Cloud condensation nucleus</td>
</tr>
<tr>
<td>SMPS</td>
<td>Scanning mobility particle sizer</td>
</tr>
<tr>
<td>CPC</td>
<td>Condensation particle counter</td>
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<tr>
<td>SFG</td>
<td>Sum frequency generation</td>
</tr>
<tr>
<td>SHG</td>
<td>Second harmonic generation</td>
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<tr>
<td>DMA</td>
<td>Differential mobility analyzer</td>
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<tr>
<td>PSL</td>
<td>Polystyrene latex</td>
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<tr>
<td>HR-ToF-AMS</td>
<td>High-resolution time-of-flight Aerosol Mass Spectrometer</td>
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<td>VFT relationship</td>
<td>Vogel-Fulcher-Tammann relationship</td>
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1. Introduction

VOCs emitted by the biosphere and anthropogenic activities react in the atmosphere with oxidants to produce secondary oxygenated products [Fehsenfeld et al., 1992; Hallquist, Wenger, Baltensperger, Rudich, Simpson, Claeys, Dommen, Donahue, George, Goldstein, Hamilton, Herrmann, Hoffmann, Inuma, Jang, Jenkin, Jimenez, Kiendler-Scharr, Maenhaut, McFiggans, Mentel, Monod, Prévôt, et al., 2009]. BVOCs are emitted at levels that far exceed those of the anthropogenic VOC emissions [A. Guenther et al., 1995a; Seinfeld & Pandis, 1998] [Atkinson & Arey, 2003; Calogirou, Larsen, & Kotzias, 1999; Martin et al., 2010]. VOC oxidation can form products with decreased volatilities as the oxygen-to-carbon ratio increases. The condensation these products results in the formation of secondary organic aerosols (SOAs) [Chan et al., 2010; Kroll & Seinfeld, 2008a]. Here aerosol is defined as a mix of gas-phase and particle-phase molecules that partition between the two phases. This partitioning is a strong function of temperature and relative concentrations between the gas and particle phase, among other factors. The particle phase of the SOA is called secondary organic material (SOM). SOMs have important effects on climate, human health and visibility [Gunthe et al., 2009; Martin et al., 2010]. On an annual average, SOMs are estimated to account for about 50% of the total fine particle (PM_{2.5}) mass globally [Baltensperger et al., 2005; Y. Gao, Hall IV, & Johnston, 2010a; Lee & Kamens, 2005; Martin et al., 2010; Seinfeld & Pandis, 2006c; Michael P. Tolocka et al., 2006; D. Zhang & Zhang, 2005]. However, formation and growth mechanisms of SOMs, and their physicochemical properties, remain insufficiently characterized for quantitative modeling at the level needed to accurately predict the climate and health related effects.
The introduction is organized as follows: Section 1.1-1.3 summarizes the current understanding of the formation mechanism of the $\alpha$-pinene derived SOMs and how their physicochemical properties are affected by the environmental parameters. Section 1.4 briefly describes the two sets of instruments that are used to study the scientific hypotheses of the thesis. Section 1.5 presents the rationale of the study and the organization of each chapter.

1.1 Monoterpene Emission and Chirality

Monoterpenes ($C_{10}H_{16}$), such as $\alpha$-pinene, $\beta$-pinene, sabinene, and limonene, are a class of important BVOC species that contribute to SOA formation. Unlike isoprene, which is emitted directly from the leaf after being produced, monoterpenes can be stored in the leaf. Their emission is affected mainly by temperature, but can also be influenced by sunlight and relative humidity (RH) [Ciccioli et al., 1997; A. B. Guenther, Zimmerman, Harley, Monson, & Fall, 1993; Schade, Goldstein, & Lamanna, 1999]. Monoterpenes are significant for SOA production due to their high emissions and the relatively low volatilities of their oxidation products. Studies have shown that monoterpenes account for 10-50% of the global BVOC emissions [A. Guenther et al., 1995c; Kanakidou et al., 2005], comparable to the 150 TgC year\(^{-1}\) total anthropogenic VOCs, including the fossil fuels and biomass burning [Muller, 1992].

Monoterpene concentrations vary at different parts of the world. Boreal forest and broad leave trees are famous for emitting a significant amount of monoterpenes, Figure 1-1 [Stavrakou et al., 2012]. The European boreal forest has a concentration between 0.17-0.64 ppm during the summer time [Eerdekens et al., 2009; Sellegrí, Hanke, Umann, Arnold, & Kulmala, 2005], and the concentration in the Amazon rainforest changes
Introduction

Figure 1-1 Global monoterpane emission in July 2009 from the MEGAN inventory.

Unit: µg C m\(^{-2}\) s\(^{-1}\). Adopted from Stavarkou et al. [2011].

from 0.2-1.0 ppm [Yáñez-Serrano et al., 2015], depending on the temperature, sunlight, and meteorological conditions. Most of the monoterpane species also have stereoisomers, i.e., these isomers that have the same chemical formula and atom connectivity but different spatial orientation of their atoms such that they cannot be structurally superimposed. The most abundant monoterpane, α-pinene, has two stereoisomers, namely (+)- and (−)-α-pinene (absolute configurations (1R,5R) and (1S,5S) α-pinene, respectively) as shown in Figure 1-2. Both compounds have exactly the same mass, boiling point, freezing point, and density. These stereoisomers have quite distinctive ratios depending the geographical location. The ratios of (+)-α-pinene to (−)-α-pinene have been measured by GC-MS to be 1:2 to 1:1 and 3:1 from Amazon tropical
Figure 1-2 Molecular structures of the two enantiomers of α-pinene.

forests, an oak forest, and a boreal forest, respectively [Song, Staudt, Bourgeois, & Williams, 2014; Williams, Yassaa, Bartenbach, & Lelieveld, 2007]. The total concentration fluctuates between 0.1-0.5 ppm at different measurement sites. The effects of the chiral nature of α-pinene on its SOM properties will be discussed in Section 1.2 and Chapter 3.

α-pinene readily reacts with ozone to form secondary products under ambient conditions. Ozone attacks the double bond in α-pinene forming an energized Criegee intermediate that can follow two possible pathways: quenching to form a stabilized Criegee intermediate or rearrangement to form a hydroperoxide. The stabilized intermediates from either pathway can form end products through degradation, isomerization, and reaction with other atmospheric species such as water [Kroll & Seinfeld, 2008c].

The oxidation process of other monoterpenes is very similar to that of α-pinene described above. Because of the importance of monoterpenes in the SOM formation process, α-pinene is a suitable compound to study the formation of SOM from BVOCs and their physicochemical properties.
1.2 Formation of Secondary Organic Material Particles

The products from BVOC oxidation can form new particles either through particle nucleation or partitioning to existing particles. Particle nucleation is generally defined as creation of molecular embryos or clusters prior to formation of a new phase during the transformation of vapor to liquid and then to solid [R. Zhang, Khalizov, Wang, Hu, & Xu, 2012]. This process involves a decrease in both enthalpy and entropy of the nucleating system, which are thermodynamically competing processes. On a molecular scale and a short timescale, gas molecules collide with each other to form small clusters during nucleation. A free energy of cluster formation, $\Delta G = \Delta H - T \Delta S$, is often used to characterize this process. As illustrated in Figure 1-3 [Dalmaschio, Ribeiro, & Leite, 2010], $\Delta G$ increases with cluster size before reaching a maximum at the critical cluster size, after which the spontaneous nucleation happens. For homogeneous nucleation, the minimum particle diameter $d_P$ after nucleation is influenced by the supersaturation extent of the gas phase species, which can be related to the Kevin equation (Eq. 1-1):
\[ d_p = \frac{4\sigma v_i}{kT \ln S} \]  

(1-1)

where \( \sigma \) is the surface tension of the particle, \( v_i \) is the volume of the particle, \( k \) is the Boltzmann constant \((1.38 \times 10^{-23} \text{ J K}^{-1})\), \( T \) is the temperature and \( S \) is the supersaturating ratio.

Particle phase partitioning assumes that SOM particles comprise a mixture of semivolatile organic compounds that partition between the gas and particle phases [Hallquist, Wenger, Baltensperger, Rudich, Simpson, Claeys, Dommen, Donahue, George, Goldstein, Hamilton, Herrmann, Hoffmann, Iinuma, Jang, Jenkin, Jimenez, Kiendler-Scharr, Maenhaut, McFiggans, Mentel, Monod, Prévôt, et al., 2009; Odum et al., 1996]. The equilibrium partitioning coefficient, \( K_{p,i} [N. M. Donahue, Robinson, Stanier, & Pandis, 2006] \), determines the partitioning of each compound (Eq. 1-2):

\[ K_{p,i} C_{oA} = \frac{C_i^P}{C_i^g} = \frac{C_{oA}}{C_i^*} \]  

(1-2)

where \( C_i^g \) is the mass concentration of species \( i \) per unit volume of air (\( \mu \text{g m}^{-3} \)) in the gas phase, \( C_i^P \) is the mass concentration per unit volume of air (\( \mu \text{g m}^{-3} \)) in the particulate phase, \( C_{oA} \) is are the mass concentration per unit volume of air (\( \mu \text{g m}^{-3} \)) of the total absorbing particle phase, and \( C_i^* \) is the saturation vapor pressure.

The fraction \( F_i \) of a semivolatile compound in the particle phase can be calculated from equation 1-3:

\[ F_i = \frac{C_{oA} K_{p,i}}{1 + C_{oA} K_{p,i}} = \frac{1}{1 + C_i^*/C_{oA}} \]  

(1-3)
Equation 1-3 shows that the higher the saturation vapor pressure is, the less organics that tend to stay in the particle phase. The amount of absorbing material also affects the organic compound distribution between the particle phase and the gas phase, i.e., the more absorbing material, the more organic compounds are in the particle phase. To help characterize the large number of organic products produced from VOC oxidation, the volatility basis set (VBS) approach was developed [N. M. Donahue et al., 2006; Presto & Donahue, 2006]. In this approach, VOC oxidation products are divided into 9 bins of different saturation vapor pressures, with each bin separated by one order of magnitude. Different SOA reaction products can be mapped to the same bins while maintaining the mass balance. The VBS approach can represent particle mass concentration with a broader range (0.1–100 µg m\(^{-3}\)) and at the meantime provide information about the distribution of organic compounds in the gas phase.

However, even though the vapor pressures of the first generation oxidization products of \(\alpha\)-pinene ozonolysis are significantly lower than the pure \(\alpha\)-pinene, their vapor pressures are still high enough that those compounds should primarily remain in the gas phase. Studies have shown that further oligomerization processes of these products are needed to create molecules that have sufficient low volatility to partition into the particle phase and form SOMs [Hall & Johnston, 2011]. Given that the stereoisomers can potentially affect the oligomerization process through their mirror-imaged structures, different ratios of the chiral enantiomers of \(\alpha\)-pinene may result in SOM with different physical properties. This will be mainly discussed in Chapter 3.
1.3 Effects of Phase and Diffusivity on Particle Growth and Reactivity

Dynamic viscosity, $\eta$, is a physical quantity used to describe the fluidity of a substance. A decreasing dynamic viscosity not only represents a reduction in the macroscopic transportation of the liquid, i.e., fluidity, but also implies a decreasing mass transportation ability for other molecules in the liquid, such as diffusion. If the diffusion coefficient of a molecule in the liquid is defined as $D$, the relationship between the molecular diffusion coefficient and the liquid dynamic viscosity can be expressed in the form of Einstein-Stokes Equation (Eq 1-4).

$$D = \frac{kT}{6\pi r\eta} \quad (1-4)$$

where $k$ is the Boltzmann constant, $T$ is the absolute temperature, $r$ is the effective radius of the diffusing molecule. When the $r$ is set to be 1 nm, the viscosity and the diffusion coefficient of molecules within common substances are shown in Figure 1-4 [Thomas Koop, Johannes Bookhold, Manabu Shiraiwa, & Ulrich Poschl, 2011a].

Based on the dynamic viscosity values in Figure 1-4, the substances can be categorized into three main categories: liquid ($<10^2$ Pa s), semi-solid ($10^2$-$10^{12}$ Pa s) and solid ($>10^{12}$ Pa s) [Thomas Koop et al., 2011a]. Substances with a dynamic viscosity larger than $10^{12}$ Pa s are usually glasses, i.e., non-crystalline amorphous solids without long-range molecular order [Angell, 1995; Debenedetti & Stillinger, 2001]. A liquid can become a glass by cooling quenching, rapidly drying out from organic solutions or vapor deposition under low temperatures [Thomas Koop et al., 2011a]. The temperature (or temperature interval) where a liquid becomes glass is called the glass transition
temperature, $T_g$. It is important to note that the Stokes Einstein Equation usually does not hold when the substance undergoes glass transition.

**Figure 1-4** The dynamic viscosity and diffusion coefficient of various substances. The upper panel shows the dynamic viscosity values and corresponding values to the classification of solid, semi-solid and liquid. The lower panel shows the e-fold diffusion time of a 1 nm molecule as a function of particle diameter. Adopted from Koop et al. [2011].

The phase and viscosity of atmospheric aerosol particles composed of SOM have important implications for the growth, aging, and ultimate fate of SOM-containing particles [Vaden, Song, Zaveri, Imre, & Zelenyuk, 2010; Virtanen et al., 2010].

Traditionally, SOM particles are viewed as low viscosity droplets where the gas species from the surrounding environment diffuse quickly into the droplets and reach instant equilibrium [N. M. Donahue et al., 2006], though recent work demonstrated a higher
viscosity and lower diffusion coefficient than what was assumed [Kidd, Perraud, Wingen, & Finlayson-Pitts, 2014a; Price et al., 2014; Renbaum-Wolff et al., 2013f; Vaden et al., 2010; Virtanen et al., 2010]. An overestimated diffusion coefficient can result in over-prediction of aerosol particle mass concentration, as reported recently by Shiraiwa and Seinfeld [Shiraiwa & Seinfeld, 2012]. Studies also show that particle aging processes [Shiraiwa, Ammann, Koop, & Pöschl, 2011b; Shiraiwa & Seinfeld, 2012], particle number concentrations, and mode diameters [Riipinen et al., 2011; Shiraiwa, Yee, et al., 2013] are influenced by diffusion coefficients and aerosol growth processes, all of which can affect air quality and climate predictions. A detailed study of the phase and diffusion of SOM and how this would affect the chemical reactivity is discussed in Chapter 4 and 5.

1.4 Water-Jacketed Flow Tube Reactor and the Aerosol Particle Mass Analyzer

Tube Reactors have been widely used to conduct atmospheric chemistry studies. Compared with smog chambers, flow tube reactors have the advantage of producing particles within a relatively short time frame with large mass loading for coagulation related studies or sample collection. Nevertheless, the high precursor concentrations, increased wall effects and short residence times employed in the flow tube reactor can produce SOMs whose composition can potentially deviate from those produced under ambient conditions. Therefore the flow tube reactor is generally useful for relatively fast reactions and reactive uptake studies [Y. Q. Gao, Hall, & Johnston, 2010; Tolocka, Saul, & Johnston, 2004]. Several α-pinene oxidation studies involving using a flow tube reactor to study SOM particle composition and mass yield are listed in Table 1-1
<table>
<thead>
<tr>
<th>Author</th>
<th>α-pinene Conc (ppm)</th>
<th>Ozone Conc (ppm)</th>
<th>Residence Time (s)</th>
<th>Particle Number Conc (cm$^{-3}$)</th>
<th>Particle Mass Conc (µg m$^{-3}$)</th>
<th>Mode Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tolocka et al.</td>
<td>83</td>
<td>1</td>
<td>3</td>
<td>6.50×10$^5$</td>
<td>15</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>1</td>
<td>22</td>
<td>2.10×10$^6$</td>
<td>95</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>136</td>
<td>1</td>
<td>3</td>
<td>4.00×10$^6$</td>
<td>36</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>136</td>
<td>1</td>
<td>22</td>
<td>5.90×10$^6$</td>
<td>400</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>43</td>
<td>0.2</td>
<td>23</td>
<td>1.50×10$^6$</td>
<td>3.5</td>
<td>34</td>
</tr>
<tr>
<td>Jonsson et al.</td>
<td>0.019</td>
<td>1.18</td>
<td>242</td>
<td>1.20×10$^4$</td>
<td>2</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>0.024</td>
<td>1.11</td>
<td>242</td>
<td>6.00×10$^3$</td>
<td>2</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>0.023</td>
<td>1.17</td>
<td>242</td>
<td>1.00×10$^4$</td>
<td>0.6</td>
<td>N/A</td>
</tr>
<tr>
<td>Gao et al.</td>
<td>43</td>
<td>0.24</td>
<td>23</td>
<td>3.90×10$^6$</td>
<td>14</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>43</td>
<td>0.3</td>
<td>23</td>
<td>9.30×10$^5$</td>
<td>49</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>43</td>
<td>0.45</td>
<td>23</td>
<td>2.70×10$^6$</td>
<td>187</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>43</td>
<td>0.55</td>
<td>23</td>
<td>3.70×10$^6$</td>
<td>279</td>
<td>49</td>
</tr>
<tr>
<td>Winkler et al.</td>
<td>90</td>
<td>N/A</td>
<td>30</td>
<td>3.00×10$^4$</td>
<td>N/A</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>N/A</td>
<td>30</td>
<td>2.00×10$^5$</td>
<td>N/A</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>N/A</td>
<td>30</td>
<td>5.00×10$^6$</td>
<td>N/A</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 1-1 Summary of literature experimental conditions and observations on flow tube reactor.
Introduction

[Y. Gao et al., 2010a; A. M. Jonsson, Hallquist, & Ljungstrom, 2008; Åsa M. Jonsson, Hallquist, & Ljungström, 2005; M. P. Tolocka et al., 2006; Winkler et al., 2012]. A flow tube reactor is constructed based on the previous literature data and the details of the reactor will be discussed in Chapter 2.

The Aerosol Particle Mass Analyzer (APM) was first invented in 1996 [Ehara, Hagwood, & Coakley, 1996]. A schematic of the APM is shown in Figure 1-5. The instrument consists of two cylindrical electrodes with voltage \( \phi \) that rotate at the same angular velocity \( \omega \). There is a narrow angular space between the outer electrode and the inner electrode, where charged ambient particles pass through. The particles are subjected to the centrifugal force and the electrostatic force while they are inside the angular space. Only particles with mass \( m_p \) meet the following equation can exit the instrument:

\[
m_p = \frac{4qe\phi}{\omega^2 (L_2 + L_3)^2 \log(L_2 / L_3)}
\] (1-5)

Here, \( q \) is the number of charges on a particle, \( e \) is the elementary charge value, and \( L_1 \) and \( L_2 \) are respectively the inner and outer radius of the cylindrical channel that allows particles to pass through in the APM [Ehara et al., 1996; M. Kuwata & Kondo, 2009]. APM is widely used for measuring the particle mass, because the mass measured is not
subjected to the influence of particle diameter or other parameters. When the voltage and
the angular speed is measured accurately, the detection limit at the femtogram level can
achieved. This corresponds to the mass of the nanoparticles. The use of the flow tube
reactor and APM instrument will enhance the ability to produce fresh SOM and
determine aerosol physicochemical properties with other aerosol instruments.

1.5 Motivation and Organization of Thesis

SOMs produced from oxidation of BVOSc exceed the amount of biogenic and
anthropogenic sulfate aerosols combined [Andreae & Crutzen, 1997]. They have
important climate effects such as scattering sunlight and acting as cloud condensation
nucleus (CCNs), and also have implications for human health. The effects are governed
by particle phase, size, and composition, which ultimately are all influenced by
physicochemical properties of aerosols [Hallquist, Wenger, Baltensperger, Rudich,
Simpson, Claeys, Dommen, Donahue, George, Goldstein, Hamilton, Herrmann,
Hoffmann, Inuma, Jang, Jenkin, Jimenez, Kiendler-Scharr, Maenhaut, McFiggans,
Mentel, Monod, Prévôt, et al., 2009; M. L. Smith, You, Kuwata, Bertram, & Martin,
2013]. However, our understanding of these properties of the aerosols is incomplete,
especially regarding the role of precursors and the particle viscosity in altering SOM
properties. This thesis aims to advance the knowledge in these areas mentioned above in
order to provide better understanding in the growth, reactivity, and aging of SOM-
containing particles.

The thesis is organized as follows. Chapter 2 describes the operation of the flow tube
reactor for the experiments and quantitatively explains the mass and number
concentrations as well as the time evolution of the SOM produced from the flow tube
under different conditions. Chapter 3 proposes the hypothesis of how precursor chirality affects the physical properties of the aerosol particles, and uses a series of experiments to verify the hypothesis proposed by combining the optimum conditions found in Chapter 2. Chapter 4 uses the flow tube reactor and APM to study the phase state and viscosity of SOMs under different RH conditions, and explains the effects of viscosity on aerosol chemical reactivity properties. Chapter 5 provides the joint collaboration results of how water and aerosol phase states affect particle phase diffusivity as well as the surface molecular arrangement. Those aerosol samples are collected from the flow tube reactor and undergo further spectroscopy measurements by our collaborators. Chapter 6 summarizes the main findings of in the thesis.
2. Production of Secondary Organic Material in a Flow Tube Reactor

2.1 Introduction

SOA particles are an important class within the atmospheric aerosol budget, on average accounting for about 50% of the annual total PM$_{2.5}$ [Brindza & Walker, 2009; Avram M. Buchbinder, Eric Weitz, & Franz M. Geiger, 2010]. However, the production mechanisms, as well as the physicochemical properties of the SOM constituting the particles, remain insufficiently characterized and poorly understood for quantitative modeling at the level needed for accurate predictions of their effects on climate, human health, and visibility. This knowledge gap has motivated many recent research efforts for the characterization of SOA particles and the SOMs that constitute them [Brindza, Ding, Fourkas, & Walker, 2010; Horng, Brindza, Walker, & Fourkas, 2009; G. Li, Dhinojwala, & Yeganeh, 2009; Nihongyanagi, Miyamoto, Oldojiri, & Uosaki, 2004; Sefler, Du, Miranda, & Shen, 1995].

Herein we prepare submicron sized SOA particles from the ozonolysis of a dominant monoterpene, α-pinene, in a flow tube reactor, which enables the rapid synthesis of aerosol particles for a variety of particle number and mass concentrations. Given that an SOM is ultimately derived from gas phase molecules, the diameter and mass of SOA particles are directly coupled to particle growth. Through the analysis of particle size distributions prepared under twenty different reaction conditions, we determined when particles are mainly produced from nucleation and condensation and when they are formed mainly from coagulation.
2.2 Experimental

2.2.1 Configuration of the Flow Tube Reactor

The flow tube reactor used in this work consisted of three parts (Figure 2-1). The first part involved the production and dilution of gases, which was controlled using four mass flow controllers (MKS, M100B Model). A flow of air from an Aadco 737 pure air generator passed through an ozone generator (Jelight, Model 1000), producing 200-500 ppm of ozone at flow rates ranging from 0.3 to 3 sLpm. Ozone concentrations were controlled and adjusted to the desired levels by dilution in dry air at various flow rates. α-
Pinene was introduced into the flow tube via an additional flow of pure air at 0.50 sLpm passed through a syringe injector system (CHEMYX, Fusion Touch 200 Model) that was heated to 135 ± 1 °C. The syringe contained a 1:1 mixture of (+)- and (−)-α-pinene (Sigma-Aldrich, ≥99% purity, 97% enantiomeric excess) in excess 2-butanol (Sigma-Aldrich, ≥99.5% purity) at a dilution ratio of 1:624 [Heuchel et al., 1993; G. Li et al., 2009; Sefler et al., 1995], which was used as an OH scavenger to ensure that ozonolysis was the only reaction occurring inside the flow tube. The concentration of α-pinene in the flow was adjusted by changing the syringe injection rate. A control experiment carried out using pure 2-butanol under the same ozone concentration led to no particle production.

The second part of the setup comprised of precursor injector and the glass tube, which had an inner diameter of 48.2 mm and length of 1.30 m. The flow tube was operated slightly above ambient pressure, around 25 °C, in the laminar flow regime (Reynolds number of 9.4 ± 0.5), and with a residence time of 38 ± 1 s [Ng et al., 2006]. The ozone and α-pinene concentrations reported here are relevant for the conditions at the inlet of the flow tube. We calculated the concentrations for each experiment from the combination of flow rates and dilution steps described above. As shown in Figure 1, the ozone and α-pinene flow inlets were arranged perpendicularly to each other to induce turbulence at the injection point and thus promote rapid mixing. The inlet of the flow tube was equipped with an ozone sensor (Ecosensors, UV-100) and a temperature sensor (National Instrument, USB-TC01). The temperature was measured to be 25 ± 1 °C over the course of the several hours it took to perform individual experiments. The total
pressure inside the flow tube was measured using a baratron (Omega PX409) and ranged from 1.00 to 1.01 atm.

The third part of the setup consisted of an outlet that was split between sample collection and size distribution measurements. The particles were collected on Teflon filters (Sartorius Stedium, 47 mm diameter, part #11807-47-N, 200 nm pore size, collection efficiency of 95%) at a sampling rate of 1.82 sLpm. Particle number-diameter distributions were measured using a Scanning Mobility Particle Sizer (SMPS, TSI, 3934 Model) [Pawlowski, 2007]. Integrated number concentrations were measured using a condensation particle counter (CPC, TSI Incorporated, 3022 Model) up to a detection limit of $10^7$ particles cm$^{-3}$. To calculate the mass concentration of collected particles on the filters, a material density of 1200 kg m$^{-3}$ was used [Charoensaeng, Sabatini, & Khaodhiar, 2009]. By varying the collection time and the reaction conditions, filter samples of variable mass loadings and number concentrations were collected and subsequently analyzed.

2.2.2 Effect of Precursor Concentration on particle production

The effects of precursor concentrations are explored in this set of experiments. The ozonolysis reaction of $\alpha$-pinene only has two reactants and the concentrations of both reactants are varied within a predefined range. Existing literature and the natural range of our injection system helped define the final concentrations of $\alpha$-pinene and ozone [Y. Gao et al., 2010a; King et al., 2010; Lee & Kamens, 2005; M. P. Tolocka et al., 2006; D. Zhang & Zhang, 2005]. Ozone injection is achieved by combining an ozone generator and a pure air dilution line, which can change the ozone concentration from 0.10 ppm to 500 ppm. The $\alpha$-pinene injection was achieved by using a syringe injection pump or a
bubbler. The syringe injection used a CHEMYX, Fusion Touch 200 Model syringe pump to inject a diluted α-pinene solution to the α-pinene vaporizer. The function of the vaporizer is to vaporize the liquid droplet to the gas form and then carried to the flow tube reactor. This setup is ideal for low α-pinene concentrations ranging from 0.125 ppm to 5 ppm. Higher concentrations of α-pinene injected through the syringe pump tended to vaporize slowly in the vaporizer and left residues as a result. Thus for this set of experiments, a bubbler was also used to induce bubbles in the pure α-pinene liquid and bring gas to the reactor. The bubbler is not as precise as the syringe injection, but can achieve a higher concentration of 5-10 ppm. By combining these techniques, the α-pinene concentrations had four levels: 0.125 ppm, 1.00 ppm, 10.0 ppm and 100 ppm. The ozone concentrations had 5 different levels, 0.10 ppm, 1.0 ppm, 5.0 ppm, 50.0 ppm and 500 ppm. SMPS was used to measure the number concentration, mass concentration, mean diameter and other parameters of the aerosol group. All the method listed above generated and measured SOM particles ranging from nearly zero concentration to $10^7$ cm$^{-3}$, spanning over seven orders of magnitude. The influence of precursor concentrations was studied with a data calculation routine developed using Mathematica 8.1 (Wolfram Research, Inc.). The routine consisted of reading the data file, selecting the input data, converting the data to number concentration, plotting the result in a single line plot and multiple line plots. The results are shown in Section 2.3.2.

2.2.3 Effect of Residence Time on particle production

As an experimental demonstration of the importance of condensational growth for our reaction conditions, an experiment with a longitudinally movable particle sampler was conducted using 50 ± 1 ppm of ozone and 125 ppb of α-pinene. The reason for
choosing this specific concentration was to analyze the influence of residence time on condensational and coagulational growth, as well as the particle growth dynamics. By varying the position of the particle sampler in the flow tube reactor, the particle size distributions can be analyzed at various times during the whole evolution process, thus allowing the dynamics to be studied. The position of the particle sampler inside the flow tube is then translated to a reaction time using the known flow speed, which allows us to determine particle size distributions at various residence times between 3 ± 0.2 and 38 ± 1s.

2.2.4 Particle Collection

Once the particles exit the flow tube reactor, they are either sent to various analyzing instruments or the particle collection filter. The particle collection filter is made from stainless steel and consists of two parts: the upper screw cap and the lower filter holder. The lower filter holder has a mesh with 47mm diameter on top and a base which supports the mesh. Before the collection takes place, all the components of the filter collector were rinsed with methanol and water. After all parts were dried with a gentle flow of pure nitrogen, a 47-mm Teflon filter was placed on top of the mesh to allow particle collection. The upper and lower parts of the collector are then screwed together. The collection used a flow of 1.8 Lpm to 2.0 Lpm, which can achieve maximum particle collection given the total flow tube flow rate of 3.5 sLpm.

2.3 Results and Discussion

2.3.1 Distinguishing two particle growth mechanisms
Several $\alpha$-pinene oxidation studies exist that focus on SOA particle composition and mass yield, as shown in Table 1-1 [Brindza et al., 2010; Y. Gao et al., 2010a; Hayes, Keeley, & Geiger, 2010; Heuchel et al., 1993; Horng et al., 2009; A. M. Jonsson et al., 2008; Åsa M. Jonsson et al., 2005; Kweskin, Komvopoulos, & Somorjai, 2005; G. Li et al., 2009; Sefler et al., 1995; M. P. Tolocka et al., 2006; Winkler et al., 2012]. This study explored ozone concentrations that are lower than those published in the literature, except for the work of Jonsson et al.[Å M. Jonsson, Hallquist, & Ljungström, 2008], but employs residence times in the flow tube that are quite similar to those other studies. Here, we hypothesized that the lower and higher concentrations employed in the present study would be useful for constraining modeling of nucleation and growth processes accompanying particle production by $\alpha$-pinene ozonolysis. The goal of the experiments was to (1) characterize the SOM particles produced from the flow tube reactor at various

Figure 2-2 Comparison of the particle growth mechanisms (condensation and coagulation) and the implications.
precursor concentrations (2) identify particles mainly grown in the two different regimes, and use the particles grown in these two regimes to perform subsequent experiments. At lower concentrations, we hypothesized the particles grew mainly from nucleation and condensational growth (Figure 2-2a). Due to the nature of the condensational growth, the semi-volatile components gradually condense on to the existing particle surface. The interactions between the particle phase and the gas phase during the condensational growth period are preserved and can therefore be analyzed through lab instruments. In contrast, the particles grown from coagulation-driven growth will have had constant collisions with each other. The numerous collisions will have forced the particle components to mix with each other and thus erase any evidence of interactions between the particle phase and the gas phase, as shown in Figure 2-2b. Coagulation growth regime

<table>
<thead>
<tr>
<th>O$_3$ (ppm)</th>
<th>α-pinene (ppm)</th>
<th>0.15±0.02</th>
<th>0.9±0.1</th>
<th>5.7±0.2</th>
<th>43±1</th>
<th>194±2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.125</td>
<td>N/A</td>
<td>9.5</td>
<td>1.5</td>
<td>0.20</td>
<td>0.044</td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>8.5</td>
<td>N/A</td>
<td>1.5</td>
<td>0.20</td>
<td>0.044</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>0.85</td>
<td>0.85</td>
<td>N/A</td>
<td>0.20</td>
<td>0.044</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>0.085</td>
<td>0.085</td>
<td>0.085</td>
<td>N/A</td>
<td>N/A</td>
<td></td>
</tr>
</tbody>
</table>

The limiting reactant can be ozone or α-pinene depending on which was in excess. Entries of “N/A” indicate that the reaction conditions were pseudo-first order neither in ozone nor in α-pinene. A bimolecular rate constant of $8.70 \times 10^{-17}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ was used [Atkinson, Hasegawa, & Aschmann, 1990]. A residence time of 38 ± 1 s was used.
need to be studied, too, because it is suitable for the research in Chapter 4 that requires to form non-spherical particles.

Another parameter that helps categorize the particle growth regime is the half-life time of the limiting reagent. The half-life time is useful in estimating the extent of the reactions thus give information of the relative amount of the gas phase products. Given the current reaction condition, assuming the ozonolysis of $\alpha$-pinene is second-order, the half-life of the limiting reagent can readily be computed under pseudo-first order conditions. From this calculation, we estimated the extent of the reaction as the ratio of the half-life of $\alpha$-pinene or ozone to the flow tube residence time (Table 2-1). For an ozone concentration equal to or greater than 43 ± 1 ppm, the half-life of $\alpha$-pinene was calculated to be ten times smaller than the residence time, indicating $\alpha$-pinene reacted to completion near the entrance of the flow tube. For these conditions, nucleation of new particles and growth by coagulation of the particles are expected to occur in spatially distinct parts of the flow tube (cf. section 2.3.2). For the rest of the conditions, the $\alpha$-pinene oxidation simultaneously happens throughout the flow tube and causes the nucleation in inside the flow tube reactor. The nucleated particles undergo coagulation within the existing particles throughout the flow tube and makes coagulation the primary causes for the particle growth.

2.3.2 Mass and Number Concentrations of the Particle Populations

To this end, we explored a matrix of reaction conditions summarized in Table 2-2 which shows that the number and mass concentrations of the particles produced increased with $\alpha$-pinene and ozone concentrations. As shown in Table 2-2, these conditions produced $(4.4 \pm 0.6)$ to $(6.3 \pm 0.7) \times 10^5$ particles cm$^{-3}$ and mass concentrations of $10^1$ to
10^4 \mu g m^{-3}, respectively, depending on reaction conditions. The reaction conditions described here produced particle concentrations that were stable over the course of several hours (e.g., mean value of 3.30 \times 10^5 cm^{-3} and standard deviation of 0.13 \times 10^5 cm^{-3}; cf. Figure 2A).

Figure 2-3 shows number-diameter distributions for particles produced using $\alpha$-pinene precursor concentrations ranging from 0.125 $\pm$ 0.003 to 10.0 $\pm$ 0.3 ppm and a fixed ozone concentration of 43 $\pm$ 1 ppm.

After examining the number concentrations in Table 2-2, we are able to make the following conclusions: (1) the particle number concentration and mass concentration has a positive correlation with ozone and $\alpha$-pinene concentrations, and the relationship is non-linear, and (2) given that coagulation imposes an upper limit of $10^5$ to $10^6$ particles cm$^{-3}$ under the conditions relevant here [Doyaguez, Calderon, Sanchez, & Fernandez-Mayoralas, 2007], the particles are likely to
Table 2-2. The properties of SOM particles produced from the flow tube reactor under various conditions.

| O₃ (ppm) | α-pinene (ppm) | | | | |
| --- | --- | --- | --- | --- |
| 0.15 ± 0.02 | 0.9 ± 0.1 | 5.7 ± 0.2 | 43 ± 1 | 194 ± 2 |
| Num. Conc. | 0 | (1 ± 1) × 10² | (1.0 ± 0.6) × 10⁵ | (4.4 ± 0.6) × 10⁵ | (3.2 ± 0.2) × 10⁵ |
| Mass. Conc. | 0 | (3 ± 5) × 10⁻² | 15 ± 5 | 11 ± 3 | 20 ± 2 |
| Mode Diameter | 0 | 22 ± 4 | 60 ± 5 | 35 ± 3 | 34 ± 2 |
| Geo. St. Deviation | N/A | 1.2 | 1.3 | 1.3 | 1.5 |

| O₃ (ppm) | α-pinene (ppm) | | | | |
| --- | --- | --- | --- | --- |
| 0.125 ± 0.003 | 0 | | | |
| Num. Conc. | 0 | (1 ± 1) × 10² | (1.0 ± 0.6) × 10⁵ | (4.4 ± 0.6) × 10⁵ | (3.2 ± 0.2) × 10⁵ |
| Mass. Conc. | 0 | (3 ± 5) × 10⁻² | 15 ± 5 | 11 ± 3 | 20 ± 2 |
| Mode Diameter | 0 | 22 ± 4 | 60 ± 5 | 35 ± 3 | 34 ± 2 |
| Geo. St. Deviation | N/A | 1.2 | 1.3 | 1.3 | 1.5 |

| O₃ (ppm) | α-pinene (ppm) | | | | |
| --- | --- | --- | --- | --- |
| 1.00 ± 0.03 | 0 | | | |
| Num. Conc. | 0 | (3.1 ± 0.9) × 10² | (1.5 ± 0.2) × 10⁵ | (5.5 ± 0.2) × 10⁵ | (5.8 ± 0.4) × 10⁵ |
| Mass. Conc. | 0 | (9 ± 3) × 10⁻³ | 61 ± 9 | (52 ± 0.1) × 10² | (66 ± 0.1) × 10² |
| Mode Diameter | 0 | 33 ± 7 | 86 ± 6 | 84±3 | 85 ± 19 |
| Geo. St. Deviation | N/A | 1.3 | 1.4 | 1.5 | 1.7 |
Table 2-2. The properties of SOM particles produced from the flow tube reactor under various conditions (Continued).

<table>
<thead>
<tr>
<th>Num. Conc.</th>
<th>(2 ± 2) × 10^1</th>
<th>(4.0 ± 0.2) × 10^5</th>
<th>(6.0 ± 0.7) × 10^5</th>
<th>(6.3 ± 0.7) × 10^5</th>
<th>(1.8 ± 0.2) × 10^6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass. Conc.</td>
<td>10.0 ± 0.3</td>
<td>(1.6 ± 0.2) × 10^2</td>
<td>(2.5 ± 0.2) × 10^3</td>
<td>(1.19 ± 0.02) × 10^4</td>
<td>(1.57 ± 0.02) × 10^4</td>
</tr>
<tr>
<td>Mode Diameter</td>
<td>8 ± 9</td>
<td>81 ± 2</td>
<td>147 ± 9</td>
<td>245 ± 38</td>
<td>155 ± 5</td>
</tr>
<tr>
<td>Geo. St. Deviation</td>
<td>1.0</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
<td>1.5</td>
</tr>
<tr>
<td>Num. Conc.</td>
<td>(4.4 ± 0.3) × 10^5</td>
<td>(8.3 ± 0.3) × 10^6</td>
<td>(8.3 ± 0.4) × 10^6</td>
<td>(9.1 ± 0.2) × 10^6</td>
<td>(1.3 ± 0.02) × 10^7</td>
</tr>
<tr>
<td>Mass. Conc.</td>
<td>100 ± 3</td>
<td>(8.6 ± 0.1) × 10^2</td>
<td>(1.3 ± 0.1) × 10^4</td>
<td>(1.6 ± 0.04) × 10^5</td>
<td>(4.0 ± 0.1) × 10^5</td>
</tr>
<tr>
<td>Mode Diameter</td>
<td>48 ± 2</td>
<td>88 ± 5</td>
<td>134 ± 8</td>
<td>262 ± 12</td>
<td>334 ± 4</td>
</tr>
<tr>
<td>Geo. St. Deviation</td>
<td>1.4</td>
<td>1.6</td>
<td>1.5</td>
<td>1.7</td>
<td>1.9</td>
</tr>
</tbody>
</table>
grow coagulatively. Indeed, Figure 2-3 shows broadened particle size distributions for 10 ppm of α-pinene, indicative of coagulative growth, upon increasing the α-pinene concentration from 0.125 ± 0.003 to 10.0 ± 0.3 ppm. This result can be explained by the higher coagulation coefficient between large and small particles, compared to particles of similar diameter [Doyaguez et al., 2007]. (3) For lower concentrations, the particles mainly grew from condensation and nucleation while coagulation plays a minor role. As a specific example demonstrating the likelihood of condensational growth, Table 2-2 shows that an α-pinene concentration of 0.125 ± 0.003 ppm and an ozone concentration of 51 ± 1 ppm generated a particle number concentration of $(9.5 ± 0.7) \times 10^4$ cm$^{-3}$ and a particle mode diameter of 63 ± 3 nm. These conditions correspond to a calculated coagulation coefficient $K$ of $2 \times 10^{-9}$ cm$^3$ s$^{-1}$ [Ng et al., 2006]. The corresponding characteristic time for coagulation $K$ was then estimated to be 3 h, which is two orders of magnitude longer than the flow tube residence time of 38 ± 1 s. (4) For monodisperse
Production of SOM in a Flow Tube Reactor

particles and a residence time of $38 \pm 1$ s [Ng et al., 2006], particle collisions, and thus coagulation, are estimated to contribute more than 90% of the observed diameter growth for an ozone concentration of $43 \pm 1$ ppm and an $\alpha$-pinene precursor concentration of 10.0 ppm. As summarized in Table 2-2, the mode diameter and width increased for higher $\alpha$-pinene and ozone precursor concentrations under these conditions.

By examining the mass concentrations of the $\alpha$-pinene SOM generated from the experiment, the following conclusion can be drawn: (1) the mass concentration increases as the precursor concentration increases. For a given particle’s number concentration, there is an upper limit to the particle number concentration, which is determined by the coagulation constant. However, for mass concentrations, there is no such upper limit. Particles continue growing due to an increasing mass of secondary organic materials produced from the precursor. (2) the relationship between particle mass concentration and $\alpha$-pinene concentration is non-linear. This non-linear relationship can be explained by the partition theory, i.e., the partition between the gas-particle changes with the relative gas phase concentration and the vapor pressure of the species. At low precursor concentrations, the particle phase compose of low volatility products. However, as the concentration increases, in addition to the existing low volatility compounds, those products that have relatively high vapor pressure will also condense into the particle phase to form aerosol particles, causing a nonlinear increment in particle mass loading.

To sum up, coagulation and condensation growth can be distinguished from the following two aspects: (1) by comparing the size distribution of the SOA particles. The number-diameter distribution of the aerosol particles that undergo coagulation are generally broader than particles going through condensational growth. Coagulation
involves the collision between large and small particles, which naturally broadens the distribution, whereas condensation gives relatively sharp distribution curves. (2) Empirically calculate the coagulation coefficient $K$, by assuming the particles are mono-disperse and the mode diameter is the diameter of the mono-dispersed particles. The half time for coagulation can thus be deduced and compared with the residence time of the particles in the flow tube. For instance, for the 0.125 and 10 ppm concentrations shown in Figure 2-3, numerical calculations also show that particles grown from 0.125 ppm of $\alpha$-pinene have a characteristic time for coagulation $K$ of 3 h, which is much longer than the mean residence time of 38 s in the flow tube. Those particles grown from 10 ppm of $\alpha$-pinene have a characteristic time for coagulation $K$ of 10 min, which is much closer to the residence time of the flow tube than the 0.125 ppm of $\alpha$-pinene. Even so, given that the aerosol particles produced in the flow tube were not monodisperse, our calculations represent lower-limit estimates. Therefore particles produced from 0.125 ppm of $\alpha$-pinene concentration are likely going through condensational growth, whereas the particles grown from 10 ppm of $\alpha$-pinene are plausibly going through coagulation.

2.3.3 Time Evolution of Particle Population

A small plug with a similar inner diameter of the flow tube was used together with the movable sampler to measure the number-diameter distribution at different residence times. The gas injector remained stationary while the sampler was moved to different lengths within the flow tube reactor to direct the flow and sample the aerosol particles stayed in the flow tube with various residence times. The size distributions resulting from this experiment are shown in Figure 2-4. The legend of the figure shows the sampling time and the total number concentration of the particles being sampled at corresponding
times. For a residence time of 3 s, the particles produced were below the detection limit of the SMPS. For longer residence times, the mode diameter of the particle population increased from less than 10 nm to more than 50 nm. The number concentration also increased. For instance, for a residence time of $17 \pm 0.5$ s, the number concentration was $(8.6 \pm 0.5) \times 10^4$ cm$^{-3}$. For a residence time of 38 s (the original residence time of the whole flow tube), the number concentration increased to $(2.56 \pm 0.07) \times 10^5$ cm$^{-3}$. The implication of these results is that new SOM particles continued to undergo primarily condensational growth, rather than coagulation, due to an increment in both the number concentration and the particles mode mobility diameters.

![Graph showing number-diameter distributions of particle populations depending on flow tube residence time from 3 to 38 s. The shaded regions represent one standard deviation in the observed number-diameter distributions across 8-12 replicates.](image)
The particle number concentration with time and diameter plot (Figure 2-5) also shows the evolution of particle sizes over mode diameter and time. The color contour shows the particle number density from 7 nm to 80 nm and the black line shows the change of the mode diameter at different residence times. The plot shows (1) a significant growth of particles at around 25 s of residence time; (2) A steady state of particle number concentration from 25 s to 38 s; (3) The mode diameter of the particles increases as the residence time increases; (4) As the residence time increases, the density of small particles (7-20 nm) drops, indicating there is a growth of the particle from condensation rather than coagulation. If coagulation dominated the particle growth process, the density...
of small particles would not drop over time because there would be excessive new particle formation.

Having demonstrated the condensational growth conditions dominate in the above experiments, the particles were sampled by the SMPS and other instruments for further analysis. We also studied particles formed under the coagulative growth conditions. Both types of particles were collected on the 47 mm Teflon filter and subsequently analyzed by various off-line techniques.

2.4 Conclusions

SOA particles were produced in a flow tube by the ozonolysis of α-pinene at various precursor concentrations. The flow tube approach presented here allows us to prepare SOA particles under condensational growth vs. coagulative growth conditions. The approach also reduces the time for particle collection onto Teflon filters for off-line spectroscopic analysis from days in the Harvard Environmental Chamber (HEC) [C. J. Ebben, Zorn, et al., 2011a; Stanners et al., 1995] to seconds and minutes in the flow tube. The aerosol in the outflow was analyzed by SMPS to provide the particle size distribution, number concentration, and mass concentration. The particles were then collected on Teflon filters for offline analysis by vibrational sum frequency generation (SFG) spectroscopy in order to characterize their surfaces.

In the context of aerosol particle surface science, the conditions of SOA particle growth are particularly important: under condensational growth conditions, processes such as physisorption and surface (i.e., heterogeneous) chemical reactions dominate the growth processes, whereas coagulative growth conditions are more sensitive to physical and mass transfer processes. We found that depending on the ozone and α-pinene
concentrations, conditions in the flow tube reactor could be adjusted to produce particles with a wide range of well-defined number concentrations and mass concentrations in the condensational growth and coagulative growth modes. Particles with sizes of 93 ± 3 nm, prepared using 51 ± 1 ppm O\textsubscript{3} and 1.0 ± 0.03 ppm α-pinene, were formed in the flow tube under mainly coagulative growth conditions at particle number concentrations of (1.1 ± 0.1) \times 10^6 \text{ particles cm}^{-3} with a total mass of 1.2 ± 0.1 mg m^{-3}. Particles with sizes of 63 ± 3 nm, prepared using 51 ± 1 ppm O\textsubscript{3} and 0.125 ± 0.001 ppm α-pinene, were present in the flow tube at particles densities of (9.5 ± 0.7) \times 10^4 \text{ particles cm}^{-3} with a mass concentration of 12 ± 2 \mu g m^{-3}. This latter set of precursor concentrations produced mostly condensationally grown particles, whereas coagulative conditions becomes important for particles prepared using the higher ozone concentrations.
3. Physicochemical Properties of Secondary Organic Material Derived from Stereoisomers of α-pinene

3.1 Introduction

As one of the most-abundant monoterpenes, α-pinene has chiral enantiomers too, which results in an interesting situation in which forests show a stable enantiomeric ratio in biogenic emissions of monoterpenes depending on geographic location [Bohlmann, Steele Cl Fau - Croteau, & Croteau; Phillips, Savage, & Croteau, 1999; Phillips, Wildung, Williams, Hyatt, & Croteau, 2003; Stephanou, 2007; Williams et al., 2007; Yassaa, Brancaleoni, Frattoni, & Ciccioli, 2001]. Williams and coworkers reported that the ratio of emissions of (+)- to (–)-α-pinene is 1:2 in tropical forests whereas 3:1 in some boreal forests [Stephanou, 2007; Williams et al., 2007; Yassaa et al., 2001]. This asymmetric emission ratio, which depends on plant type and stress [A. Guenther et al., 1999; Lavoir et al., 2009], can lead to generating aerosol particles with the corresponding stereoisomer ratios. If these chiral aerosol particles show a difference in climate related properties, the chirality in BVOCs will affect the local climate through affecting the chirality of SOM particles.

The presence of chirality in a substance can be anticipated to have important effects on its chemical reactivity and physical properties. There are direct implications showing that chirality affects the properties of materials. For instance, chirality affects the molecular order and long-range disorder of polymer, which subsequently determines its melting point and solubility. In addition, the rigidity and the extent of crystallinity are also determined by the chiral properties of the molecules that form it [Cotton, Wilkinson,
Physicochemical Properties of SOM Derived from Chiral α-pinene

& Gaus, 1995; Shriver, Atkins, & Langford, 1991]. Similarly, chirality can also affect the properties of tropospheric aerosol particles. However, the transformation of chiral compounds from the BOVCs into the SOA has not been well understood. Due to the prominent roles SOA plays in the climate system [B. J. Finlayson-Pitts & Pitts Jr, 2000; Jacob, 1999; Seinfeld & Pandis, 2006c; Solomon et al., 2007], it is important to identify a mechanism that can retrain the chirality from BVOCs to SOM particles. In general, the terpenes are either oxidized from ozonolysis, i.e. addition of ozone across a C-C double bond, or photoxidation, where OH radicals attack the double bond and break the

![Figure 3-1 Aldol reactions of pinonaldehyde and pinonic acid.](image)

These two species are important products of α-pinene ozonolysis and they react to form product with new stereocenters.

molecules into smaller ones [Martinez et al., 2011]. To retain the chiral centers, the molecular structures has to be intact during the oxidation process, thus ozonolysis is likely to be the only pathway that will transfer the gas phase chirality into the particle
Physicochemical Properties of SOM Derived from Chiral α-pinene

phase without breaking the molecular structure. One possible SOA formation case from terpene is that the monoterpenes oxidation products undergo chemical reactions such as aldol addition to produce dimers and oligomers, which have significantly lower vapor pressure and therefore lead to the growth of organic particles. A recent study on the reaction between 1% (v/v) concentrations of terpene stereoisomers and 10% ozone (m/m) also confirms that chirality can be preserved during this first step of ozonolysis [Cataldo, Ursini, Lilla, & Angelini, 2010]. Theoretical analysis shown in Figure 3-1 also indicates a relevant reaction pathway that can generate chiral SOA particles: the ozonolysis of α-

![Figure 3-2 Cartoon representation of the dimer formation/oligomerization through stereoisomers.](image)

pinene produces less-volatile organic compounds, such as pinonaldehyde and pinonic acid. Compared to the precursor, these products have additional oxygen-bearing functional groups yet retain the four-membered ring [Docherty, Wu, Lim, & Ziemann, 2005; Heaton, Sleighter, Hatcher, Hall, & Johnston, 2009; Kroll & Seinfeld, 2008c; M. P. Tolocka et al., 2004]. Their progressively lower vapor pressures lead to the condensational growth of the organic components of aerosol particles. If products such as the ones shown in Figure 3-1 dominate the chemical composition of the particle, then the
initial stereoisomeric mix of the BVOC reactant should determine the chiral balance of the particle. Furthermore, as shown in Figure 3-2, different configurations of the stereocenters in different enantiomers would indicate the influence of an ongoing stereochemical preference in guiding further particle-phase accretion reactions, such as oligomerization, which are important particle growth mechanisms [Kalberer et al., 2004]. The chemical mechanism mentioned above might be dominant for biogenically dominated regions, such as the Amazon Basin, and a recent study on aerosol filter samples collected at the Amazon rainforest supports the existence of chiral particles [Martinez et al., 2011].

Martinez et al. collected aerosol particles smaller than 10 µm on Teflon filters at a remote site in the central Amazon Basin. The particles were collected during the dry

Figure 3-3 False-color optical and corresponding chiral SHG images of aerosol particle material collected at tower TT34 in the central Amazon Basin. Adopted from Martinez et al. [2011].
Physicochemical Properties of SOM Derived from Chiral α-pinene

Season, which is absent of biomass burning. The chirality of these particles can be readily imaged by second harmonic generation (SHG) imaging [C. Chen, Loch, Wang, & Chen, 2003; C. J. Ebben, Martinez, Shrestha, Buchbinder, Corrigan, Guenther, Karl, Petaja, et al., 2011; C. J. Ebben, Zorn, et al., 2011c; Fischer & Hache; Kriech & Conboy, 2005]. Figure 3-3 shows that the chiral SHG responses always originated from material on the filter and most of the chiral SHG response was due to sub-10-micron particles while the contributions from larger, primary biological particles, such as polysaccharide-rich bacteria and plant debris, were relatively minor [Martinez et al., 2011]. The chiral signals from these numerous submicron particles consisting mainly of secondary organic material indicates that the chirality is probably from their BVOC precursors. Another study also confirms the above hypothesis about the chirality transferring from

![Figure 3-4 SFG spectra of blank filter (i), aerosol gas phase (ii) and SOM particles collected (iii-v) from the Harvard Environmental Chamber at different enantiomer mixing ratios.](image)

The α-pinene concentration was 23 ± 2 ppb and the ozone concentration was 300 ± 15 ppb. Adopted from unpublished result of Geiger et al.
the gas phase to the particle phase. The study comes from HEC experimental results from Martin and Geiger groups. Secondary organic material were collected on Teflon filters from the Harvard Environmental Chamber [Shilling et al., 2008] by the oxidation of 23 ± 2 ppb α-pinene stereoisomers and 300 ± 15 ppb of ozone at 25.0 ± 0.1°C, 40 ± 1% RH, and low NO$_x$ (< 1 ppb). These particles used 50 nm ammonium sulfate particles as seed particles and grew to 93 nm prior to the collection. The particles were then analyzed by examining their SFG spectra [Carlena J. Ebben et al., 2012; Martinez et al., 2011; Oh-e et al., 2004; Mona Shrestha, Yue Zhang, Carlena J. Ebben, Scot T. Martin, & Franz M. Geiger, 2013]. Figure 3-4 shows the chiral responses from the collected particles, with the integrated area representing the ratio between two enantiomers. The plot shows that the chirality from the precursor does affect the chirality of the aerosol materials, although this influence is nonlinear. The nonlinear response in the figure indicates that molecular interactions, including those that result in chemical bond formation and oligomerization [Docherty et al., 2005; Heaton et al., 2009; Kroll & Seinfeld, 2008c; M. P. Tolocka et al., 2004], are taking place and that these interactions have tendencies towards specific chemical reaction pathways that induce chirality and possibly produce helical oligomers.

According to above analysis of the chemical reactions, the most likely effects of chirality happen during the oligomerization process. The newly formed oligomers have low vapor pressure and are the key in particle nucleation. When these big molecules nucleate, the stereo-geometry may have effects on the nucleation process and subsequent condensation process. As illustrated in the plot here, the oligomers formed from a single enantiomer and mixed enantiomers have different special structures, resulting in different molecular volumes. Hence when these molecules condense, the inter-molecular
interactions would likely be different and manifest this difference in aerosol macro-properties, such as number-diameter distribution, particle surface areas, and particle volumes. Therefore the rationale for this hypothesis can be outlined as follows: oligomerization reactions between terpene oxidization products are important for forming the particle phase of atmospheric aerosols, specifically SOM [Heaton, Dreyfus, Wang, & Johnston, 2007; Kalberer et al., 2004; Kroll & Seinfeld, 2008c; Vesterinen, Lehtinen, Kulmala, & Laaksonen, 2007]. Moreover, oligomerization reactions can be influenced by chirality related reactions [Chisholm, Patmore, & Zhou, 2005; Kawasaki & Soai, 2010], which often result in nonlinear responses between the chirality of molecules in the particle phase and the ratio of uneven mixtures of stereo-isomer reactants. Consequently, we can hypothesize that just as the input of uneven mixes of chiral monomers determines the properties of polymer in materials chemistry, asymmetric chiral emission profiles of terpene emissions at different parts of the world determine the chirality of SOA particles, thereby influencing the properties of those aerosol particles, which in turn affects global climate at various degrees.

However, this kind of influence will mainly exhibit itself when particles grow from nucleation and condensational growth. If the particle number concentration exceeds certain limits, the coagulation becomes dominant thus eclipsing the effects that occur in nucleation. Therefore, an effective method needs to be established to distinguish the nucleation and condensational process from the coagulational process, which was already established in Chapter 2. This Chapter will focus on linking the chirality of the precursors to the difference in macro-properties of aerosol particles.
3.2 Experimental

In this section, we synthesized and studied SOA particles from different stereoisomeric mixes of chiral BVOCs in a flow tube constructed at Harvard. The flow tube reactor generates aerosol particles in shorter time periods and thereby allows us to explore numerous reaction conditions quickly. The experimental setup is used to screen experimental conditions and resultant aerosol particle properties, allowing us to select experimental conditions that are appropriate for the tropospherically relevant, albeit more time-intensive, chamber studies. The size distributions of the SOA particles formed in the flow tube are analyzed as a function of the stereoisomeric mix in the gas phase and the oxidant and terpene concentrations.

3.2.1 Secondary Organic Material Produced from (+), (-)-α-pinene and Their Mixtures

(+) and (-)-α-pinene (Sigma-Aldrich, ≥99% purity, 97% enantiomeric excess) mixture solutions are prepared by mixing the pure α-pinene liquids at three different ratios (98:2, 50:50 and 2:98). Since chiral enantiomers are mirror images, they would not have difference in reactivity when the enantiomer ratios are inverted. Therefore we expect 98:2 mixture should behave the same as the 2:98 mixture. Nevertheless, the impurities the (+) and (-)-α-pinene solutions may be different and are able to affect the chemical reaction processes that govern the aerosol formation. Hence the 98:2 and 2:98 mixtures are used as controls when compared with 50:50 mixtures. These mixtures are then diluted with 2-butanol, which was used as an OH scavenger to ensure that ozonolysis was the only reaction occurring inside the flow tube, at a ratio of 1:624 to prepare the solution ready for ozonolysis. The final solutions are then directed into the
5.00 ml Hamilton syringe and placed onto the syringe injector. The other operational procedures are very similar to the ones described in Chapter 2. The concentration of α-pinene in the flow is adjusted by the injection rate of the syringe. To explore the relationship between chirality and number-diameter distributions, various injection rates are studied to reach an ideal particle growth rate.

In the context of aerosol particle surface science, the conditions of SOA particle growth are particularly important: under condensational growth conditions, processes such as physisorption and surface (i.e., heterogeneous) chemical reactions dominate the growth processes, whereas coagulative growth conditions are more sensitive to physical (as opposed to chemical) and mass transfer processes. Therefore it is important to distinguish between the nucleation/condensation and coagulation modes of SOA particle formation in our flow tube, which we carry out by comparing the size distributions of the SOA particles formed under the various experimental conditions. Therefore, the reaction conditions of ozone and α-pinene precursor concentrations are optimized (e.g., matrix of experiments in Chapter 2, Table 2-2) for particle sampling under conditions of condensational growth. Our survey experiments show that the α-pinene concentration producing the largest particle diameters while avoiding a significant extent of coagulation was 0.125 ppm if the ozone concentration is held in excess. As a specific example demonstrating the likelihood of condensational growth, the result shows that an α-pinene concentration of 0.125± 0.01 ppm and an ozone concentration of 51 ± 1 ppm generates a particle number concentration of $(9.5 \pm 0.7) \times 10^4 \text{ cm}^{-3}$ and a particle mode diameter of 63 ± 3 nm. These conditions correspond to a calculated coagulation coefficient $K$ of $2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. [Ng et al., 2006] The corresponding characteristic time for coagulation was
then estimated to be 3 h, which is two orders of magnitude longer than the flow tube residence time of 38 ± 1s. Even so, given that the aerosol particles produced in the flow tube were not monodisperse, our calculations represent lower-limit estimates. In contrast, we find that ozone concentrations of 50.0 ppm and α-pinene concentrations of 10.0 ppm result in ~250 nm sized particles that we attribute to the coagulation mode. We conclude that the concentrations that result in the formation of condensation mode particles are 0.125 ppm of α-pinene and 50.0 ppm of ozone.

3.2.2 Measurements of Number-Diameter Distributions

Upon exiting the flow tube reactor, the particles are introduced into three different lines. The first line leads to a CPC (Model 3022a, TSI Incorporated), where the total number concentrations of particles are analyzed. The second line leads to the SMPS (TSI, model 3071A; CPC; TSI, model 3772), where the number-diameter distribution, volume distribution, etc. are analyzed. The third line leads to the filter collection device, which will be discussed in detail in Chapter 5.

The outlet pressure is also recorded to ensure that this pressure is higher than ambient pressure to eliminate any chance for air withdrawing.

The data are analyzed subsequently by a mathematical algorithm on Mathematica. The total particle volume concentration and number concentration are plotted against the temperature, ozone concentration and other parameters as a control to verify the reliability of the data. Then the number diameter distribution is averaged according to precursor chirality and re-plotted in ordinary scales to compare the effects of precursor chirality on SOM.
Since potential differences in number-diameter distributions for different enantiomer ratios can be attributed to thermodynamic or kinetic preferences for certain oxidation pathways and gas-to-particle partition processes. These preferences will result in compositional changes of the SOM, which can also be measured by the offline techniques such as the SFG and described in detail in Chapter 5. SFG measures the spectrum of chiral organic species of SOM collected on Teflon filters with different polarization combinations. The SFG methods will be useful for explaining possible chirality induced properties from a molecular perspective and will allow testing of the hypothesis that the ratio of α-pinene enantiomers influences the number-diameter diameter distributions of produced SOM particles.

3.3 Results and Discussion

3.3.1 Stability Analysis of the Number-Diameter Distribution of the Secondary Organic Material Particles

As previously stated, we hypothesize that the different precursor chirality will lead to the difference in number-diameter distribution of the particles. To verify this hypothesis, a control experiment is needed to test whether the number-diameter distributions for the same precursor can be stable or not. The experiment was conducted in conditions with an α-pinene concentration of 125 ± 3 ppb and ozone concentration of 21 ± 3 ppm. The ± 15 number-diameter distributions of particle populations produced by ozonolysis of (+)-α-pinene, (-)-α-pinene, and 50:50 mixtures are plotted in Figure 3-5a. Because the same concentrations were used for the ozonolysis of (+)-α-pinene and (-)-α-pinene, the number-diameter distributions of the particle population should in theory be
Physicochemical Properties of SOM Derived from Chiral α-pinene

Figure 3-5 The effects of temperature on SOM properties. (a) number-diameter distributions of α-pinene derived SOM particles with different enantiomer ratios. (b) The time series SOM volume concentration, temperature, and ozone concentration. (c) Correlation plot between volume concentration and temperature. (d) schematic design of water-jacketed flow tube reactor

identical, within experimental error. From the plot we can see, however, the distributions do not match each other, at least for this version of the experimental apparatus. The mismatch can be explained by two reasons. The first reason is the intrinsic difference in (+)-α-pinene and (-)-α-pinene compounds. The two compounds are purchased from Sigma Aldrich and may have a difference of the impurities in it, which result in the difference in the properties of the SOAs generated. The second reason is the underestimated experimental fluctuations, explained largely by the sensitivity of the results to temperature and the difficulty of maintaining temperature within the needed
Physicochemical Properties of SOM Derived from Chiral α-pinene

tolerance for the employed apparatus. The fluctuations were sufficient at this point in the research project to obscure any possible difference in the number-diameter distributions because of a possible chirality effect.

3.3.2 Properties of Secondary Organic Material with Temperature Fluctuations

Another parameter that can represent the number diameter distribution is the total volume concentration of the particles. A shift in the number diameter distribution usually affects the volume distribution, which can be quantitated and shown on charts. To explore which factor changes the particle number-diameter distribution, the time series of particle volume concentration, ozone concentration, and temperature are plotted in Figure 3-5b. A comparison of one time series to another shows that the ozone concentration has no discernible effect on particle volume concentration. This result is explained because the ozone concentration is in excess compared to the α-pinene concentration. In contrast, the time series show that changes in volume concentration correlate with changes in temperature, suggesting a causative relationship of the latter on the former. The positive correlation between the particle volume concentration and the temperature is different compared with conventional thoughts, suggesting that aerosol particle would lose mass when heated, due to the volatile nature of the SOAs. The positive correlation suggests that the formation of the α-pinene SOM is a competing process between the ozonolysis rate and the condensational rate, and the ozonolysis seems to be the dominant factor during the temperature range measured. A correlation plot, shown in Figure 3-5c, establishes that a change of 1 °C induces a change of 20% in volume concentration. This result is in agreement with a previous study that reported the nucleation rate of new particles can change 20% - 50% for one degree of temperature
Physicochemical Properties of SOM Derived from Chiral α-pinene

change [R. Zhang et al., 2012].

Table 3-1 Experimental conditions that are used to test the effects of temperature on SOM properties. BVOC, ozone concentration, and correlation coefficient between SOM volume concentration and temperature are shown in the table

<table>
<thead>
<tr>
<th>Date</th>
<th>BVOC</th>
<th>BVOC Concentration</th>
<th>Ozone Concentration</th>
<th>Correlation Coefficient R</th>
</tr>
</thead>
<tbody>
<tr>
<td>May 31st</td>
<td>(-)-α-pinene</td>
<td>5 ± 0.1 ppm</td>
<td>20 ± 2 ppm</td>
<td>0.72</td>
</tr>
<tr>
<td>June 3rd</td>
<td>(-)-α-pinene</td>
<td>5 ± 0.1 ppm</td>
<td>20 ± 2 ppm</td>
<td>0.21</td>
</tr>
<tr>
<td>June 6th-10th</td>
<td>(-)-α-pinene</td>
<td>125 ± 1 ppb</td>
<td>22 ± 2 ppm</td>
<td>0.34</td>
</tr>
<tr>
<td>June 11st-12th</td>
<td>(-)-α-pinene</td>
<td>125 ± 1 ppb</td>
<td>22 ± 2 ppm</td>
<td>0.38</td>
</tr>
<tr>
<td>June 12nd-14th</td>
<td>(+)-α-pinene</td>
<td>125 ± 1 ppb</td>
<td>22 ± 2 ppm</td>
<td>0.28</td>
</tr>
<tr>
<td>June 14th-16th</td>
<td>Mixture α-pinene</td>
<td>125 ± 1 ppb</td>
<td>22 ± 2 ppm</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Changes in volume concentration can consequently alter the number-diameter distributions of particles produced in the flow tube. To achieve fluctuations in volume concentration of less than 3%, the fluctuation in temperature must be less than ± 0.2 °C. Therefore, a temperature control box was designed and added to the flow tube system.

The new system circulates constant-temperature water between the inner and outer walls of the box so as to maintain constant temperature inside the box. The flow tube and most of the gas tubing will be placed inside the box, as illustrated in Figure 3-5d. The temperature control box will decrease the variability of the measured number-diameter distributions, so that the possible effects of chirality on the diameter of produced particles may be distinguishable. In addition, the influence of chirality on particle number-
diameter distributions at varying temperatures can also be explored by adjusting the

![Graph showing the relationship between total volume concentration and temperature.](image)

**Figure 3-6** The relationship between particle volume concentration and temperature. (a) time series plot of particle volume concentration v.s. temperature. (b) correlation plot between particle volume concentration and temperature.

temperature of the circulating water. To precisely measure the temperature, a temperature sensor (Omega) was attached into the flow tube for temperature measurement. The temperature was kept at 20.3 ± 0.1 °C.

Table 3-1 shows the experimental conditions that are used to test the influence of
temperature on particle volume concentrations. All three α-pinene solutions with different enantiomer ratios as well as two concentrations are used. Except the first experiment, all experiments show a decreasing correlation coefficient between temperature and volume concentration, indicating the influence of temperature on volume concentration is insignificant when the temperature fluctuation is controlled within 0.1 °C. For instance, Figure 3-6a shows the volume concentration v.s. temperature for enantiomeric mixed α-pinene solution. Other α-pinene solutions exhibit similar trend compared with this figure.

Table 3-2 Experimental factors that can affect particle volume concentration

<table>
<thead>
<tr>
<th>Sources</th>
<th>Sinks</th>
<th>Other factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-pinene injection</td>
<td>Wall loss inside the flow tube</td>
<td>Temperature stability</td>
</tr>
<tr>
<td>concentration</td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-pinene purity</td>
<td>Wall loss on the connecting tubing</td>
<td>Flow rate stability</td>
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<tr>
<td>α-pinene solution</td>
<td></td>
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<tr>
<td>concentration</td>
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<tr>
<td>α-pinene injection</td>
<td></td>
<td>SMPS measurement accuracy/stability</td>
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<tr>
<td>rate stability</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ozone concentration stability</td>
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</table>

From the figure, it is obvious to see that volume concentration fluctuates at a lower frequency compared with temperature fluctuation, indicating that the temperature is not the reason for the change of volume concentration change anymore. Figure 3-6b shows that the correlation coefficient R between volume concentration and temperature has decreased to 0.11, compared with the previous R = 0.53 in Figure 3-5, further suggesting that the temperature does not heavily affect volume concentration. As a result, the
fluctuation of volume concentration decreases by more than 60% compared with the data without temperature control. However, it is difficult to explain the reason that causes the remaining fluctuation after removing the effect of temperature. The possible sources of the fluctuation are listed in Table 3-2. All these sources would likely cause the volume concentration to change, but it still cannot explain the 50 minute cycle of the concentration change. One likely cause for the remaining fluctuation is the dynamic inter-correlation between particle nucleation and particle growth process. For nucleation to happen, the vapor pressure of the low-volatile species need to exceed a relatively high level, a level that is usually higher than the one at which condensation happens, due to the thermodynamic barrier to form the particle. Therefore, when nucleation happens, a lot of small particles would form and then the small particles would quickly grow to larger particles due to the high vapor pressure of the non-volatile component. The consumption of the low-volatile organics reduces the nucleation process, which reduces the number of particles that can grow in larger sizes. This will in turn increase the vapor pressure of the low-volatile organics and promote another cycle of particle nucleation. The only drawback of this explanation is that the observed cycle happens at an interval of 50 minutes, which is much longer than the 38 seconds residence time of the flow tube reactor. There might be some possible wall effects of the flow tube that can retain the information of the particles beyond the residence time of the flow tube reactor to prolong the cycle time to 50 minutes. A second hypothesis is that the cycle is caused by a slight pressure change.
from the building, which can affect the inflow rates slightly and change the nucleation rate, since particle nucleation is a very sensitive process to many parameters. For the current experimental conditions, it is difficult to rule out either possibility. Nevertheless,
these two explanations are all beyond the scope that we can control and at the meantime the fluctuation has already decreased to an acceptable range. The next-step-experiment focuses on differentiating the number-diameter distributions of particles based on their chiral precursors.

3.3.3 Properties of Secondary Organic Material from Enantomerically Mixed Precursors

![Figure 3-7 Time series particle volume concentration derived from α-pinene enantiomer mixtures and flow tube temperature fluctuation.](image)

To test the effect of chiral precursor on the formed SOA particles, a total of 15 new solutions with α-pinene and 2-butanol mixed at a ratio of 1:624 are prepared. There are five solutions for each enantiomer ratios, i.e., (+)-α-pinene, (-)-α-pinene and the 50:50 (+) and (-) mixed α-pinene. All the solutions are created in the same method.
Before conducting the experiments, all the solutions in their own category are numbered randomly, and then putting together as 5 groups, with each group consisting of three different enantiomer ratios. Each group was used in the experiment at a sequence of (+), (-) and then mixed α-pinene. The data analysis consists of two parts, the volume concentration and the number diameter distribution. The comparison within each group is performed so that the inter-group variation of the outer environmental parameters (such

Figure 3-8 Correction plot between ozone concentration and particle volume concentration of α-pinene derived SOM.
as a slight change in temperature and ozone concentration) can be controlled. The

![Figure 3-9 Number-diameter distributions of SOM particles derived from α-pinene stereoisomers with various ratios.](image)

The red, green and blue line represents the (+)/(−)-α-pinene ratios are 2:98, 50:50 and 98:2, respectively. The dashed line represent one sigma.

experiment is also conducted in the same manner for all the solutions, such as injection rate, vaporizing temperature, SOM measurement parameters to minimize random errors.
The table below summarizes the information for this set of the experiment.

The result of the total volume concentration is shown in Figure 3-8. The figure shows that over long time scale, i.e. over 7-10 days period of time, the volume concentration changes by a great amount and therefore the inter-group comparison is not feasible. Even though there are frequent changes of volume concentration within a short period, the general trend for the volume concentration is decreasing, which is due to the fact that the ozone concentration is decreasing from the reduced lamp lifetime. A correlation between ozone concentration and the particle volume concentration clearly indicates that there is a positive relationship between the ozone concentration and the total volume concentration of the SOA particles. This is in accordance with the expectation because an increasing ozone concentration leads to a more thorough reaction, which produces more VOCs. Nevertheless, unlike temperature, the ozone concentration is more difficult to adjust because of reduced lifetime of the ozone lamp, which leads to an decreasing ozone concentration as the experimental time prolongs. Even though ozone concentration cannot be maintained to be completely stable, the comparison within the same group is still feasible because the variation of the volume concentration is relatively small. In addition, for each group of experiment, the temperature change is within ± 0.1 °C and the ozone concentration is within in 1 ppm. Among all these five groups, the most stable ones are group 3 and group 5. For simplicity, the number-diameter distribution of all five groups are shown in Figure 3-9 and being discussed, even though we only pick group 5 as the main focus here. The plot shows that the standard deviation of the number-diameter distribution of the three groups
is 10%. The number diameter distribution of mixed (+) and (-)-\(\alpha\)-pinene is in between the number-diameter distributions of pure (+) and (-)-\(\alpha\)-pinene.

As mentioned above, the hypothesis that chirality would promote a role on the SOM. If it happens, the mixture of (+) and (-)-\(\alpha\)-pinene would result in a different size distribution since the chirality of (+) and (-)-\(\alpha\)-pinene is expected to make the same effect, but the mixture of them is expected to be different. Our result does not agree with the hypothesis for this group. A careful analysis of the rest of the four groups of solutions also confirms that there is no statistical significance when comparing whether the mixed \(\alpha\)-pinene solution would generate SOA with different properties compared with the pure precursor. Therefore the hypothesis does not stand.

3.4 Conclusions

The influence of the precursor chirality on the properties of the SOA particles is analyzed by comparing the number-diameter distributions and the total volume concentrations of the particles generated from various ratios of (+) and (-)-\(\alpha\)-pinene. The result shows that there is not a statistically significant difference between the precursor chiral type and the particle number-diameter distributions. Therefore chirality probably does not have a strong effect on the number-diameter distributions of the SOA particles. The result also shows that temperature and the total volume concentration of the particles exhibits a positive relationship from 24-26°C, indicating the ozonolysis chemical reactions plays a dominant role when compared with the thermodynamic process of condensation. Ozone concentration and particle volume concentration also shows a
positive relationship, which can be explained by the increasing production of SOM when more ozone is present.
4. Viscosity and Merging of Suspended Particles

4.1 Introduction

The fundamental concept of SOA formation is that these products may partition a portion on pre-existing particles when their gas-phase concentrations are below their vapor pressures or nucleate to form new particles when exceeding their vapor pressures. The processes are governed in large part by particle phase and gas-particle diffusion rates. Therefore, to numerically quantify the partition between the gas phase and particle phase, the diffusion processes between various gas phase species and particle phase species need to be accurately predicted, which remains to be one of the key challenges in the current aerosol formation modeling.

Diffusion within SOM influences whether interactions with the gaseous phase are confined to the surface region of the particle or allowed to proceed towards the interior of the particle bulk [Hallquist, Wenger, Baltensperger, Rudich, Simpson, Claeys, Dommen, Donahue, George, Goldstein, Hamilton, Herrmann, Hoffmann, Inunuma, Jang, Jenkin, Jimenez, Kiendler-Scharr, Maenhaut, McFiggans, Mentel, Monod, Prévôt, et al., 2009; Kidd et al., 2014a; Renbaum-Wolff et al., 2013f; Seinfeld & Pandis, 2006c]. Diffusion therefore has important implications for the growth, aging, and ultimate fate of atmospheric organic particle particles [Vaden et al., 2010; Virtanen et al., 2010]. Until recently, SOM particles were modeled as low-viscosity liquid droplets in which gas species from the surrounding environment diffused quickly into the droplets and rapidly reached equilibrium [N. M. Donahue et al., 2006]. More recent work, however, has indicated higher viscosities and hence lower diffusion coefficients than consistent with
Viscosity and Merging of Suspended Particles

liquid droplets [Kidd et al., 2014a; Price et al., 2014; Renbaum-Wolff et al., 2013f; Vaden et al., 2010; Virtanen et al., 2010]. An overestimated diffusion coefficient can result in over-prediction of particle mass concentrations as well as under-prediction of concentrations of gas-phase species [Shiraiwa & Seinfeld, 2012]. Particle aging processes [Shiraiwa et al., 2011b; Shiraiwa & Seinfeld, 2012], particle number concentrations [Riipinen et al., 2011], and mode diameters [Riipinen et al., 2011; Shiraiwa, Yee, et al., 2013] can also be influenced by particle diffusion, in turn influencing model predictions related to air quality and climate.

Diffusion rates in submicron secondary organic particles have been measured under dry conditions [Abramson, Imre, Beranek, Wilson, & Zelenyuk, 2013]. In the atmosphere the RH cycles from low values to high values, which can have a drastic effect on diffusion rates within particles. There have been no measurements of diffusion rates in submicron secondary organic particles for the range of RH values found in the atmosphere. To address this problem, Renbaum-Wolff et al. [Renbaum-Wolff et al., 2013f] measured the viscosity of the SOM as a function of RH and then estimated diffusion rates from the viscosity measurements using the Stokes-Einstein relationship. More recently Pajunoja at al. [Pajunoja et al., 2013] observed the shape of the aerosol particles under SEM and used the relaxation time of coalescence particles to estimate its viscosity. Power et al. [Power, Simpson, Reid, & Hudson, 2013] used the optical tweezers to estimate the viscosity of aerosol particles by observing the coalescence process. Kidd et al. [Kidd et al., 2014a] used observations of deposition patterns of particles after impaction to estimate viscosity submicron secondary organic particles at a RH of 87%. Although insightful, all of these studies had limitations. The work of
Renbaum-Wolff was limited to only the water soluble component of the SOM and used supermicron particles collected on surfaces. Uncertainties in surface-particle interactions lead to relatively large uncertainties in estimated viscosities and hence diffusion coefficients at low relative humidities. The work of Pajunoja et al. had relatively large uncertainties since the method could only determine whether the particles were aspherical or not, and the viscosity estimated from the method had an uncertain in RH of 20%.

Power et al. used supermicron aerosol droplets for the experiments and the viscosities of single, binary and ternary component Newtonian fluids rather than the ambient aerosol samples were measured. The work of Kidd et al. also had large uncertainties and was limited to only a single RH of 87%. The previous studies by Renbaum-Wolff et al. and Kidd et al. also have in common that the SOM was not studied as in situ suspended aerosol particles, and many particle properties can change upon removal of the particle from suspension.

Another challenger in acquiring the diffusion rate is the complexity nature of organic aerosol. There are hundreds gas phase and particle organic species being produced in the natural environment and only a small part of these species are identified so far. That is to say, there is no direct way to measure the diffusion coefficient of each individual species partitioning to the SOM. A more general strategy is needed to predict the diffusion coefficient of various species into the SOMs. To solve this problem, Einstein-Stokes equation is used to link the relationship between molecule size, diffusivity and particle viscosity.

In summary, despite the importance of the diffusion coefficient and viscosity of SOM-containing particles, these properties have not yet been well constrained over the
range of RH values found in the atmosphere and for submicron suspended particles. To more accurately predict the behavior of particles under atmospheric conditions, precise estimates of the RH-dependent viscosity of submicron SOM-containing aerosol particles suspended in air is needed.

The present study defines particle shape quantitatively by its aerodynamic behavior. The strategy of the experiments is to retain particles in a plenum to allow time for coagulation. Particles of high viscosity have non-spherical shapes (such as dimer-shape) after colliding with each other. As the viscosity of the particle decreases upon

Figure 4-1 Cartoon representing changes in particle shape due to coagulation and to elevated RH. (A) Scenario for an experiment using a medium concentration of α-pinene (700 ppb) in which two similarly sized particles collide to form dimer and trimer agglomerates, leading to relatively larger dynamic shape factors (rightmost to middle column). They constitute <0.25% of the total particle population. They become nearly spherical after exposure to an elevated RH (middle to leftmost column). The elevated RH decreases viscosity and allows material flow. (B) Scenario for an experiment using a high concentration of α-pinene (1000 ppb), in which several particles collide to form larger agglomerates having relatively smaller dynamic shape factors. At elevated RH, these particles also flow and become spherical.
exposure to elevated RH, the material constituting the particle flows, and the particle assumes a spherical shape in order to minimize its surface energy, as shown in Figure 4-1. A model is built to combine the shape factor change versus RH with numerical simulation (COMSOL Multiphysics) and viscosity is thereby estimated.

4.2 Experimental

4.2.1 Experimental Setup

Experimental setup is described in Figure 4-2. The particle population of α-pinene SOM was generated in a flow tube reactor [Å. M. Jonsson et al., 2008; Mona Shrestha et al., 2013]. The flow tube was made of glass and had an inner diameter of 48.2 mm and a length of 1.30 m. It was operated in a laminar-flow regime (Reynolds number of 9.4 ± 0.5) for a residence time of 38 ± 1 s. The flow tube was equipped with ozone (Ecosensors, UV-100) and temperature sensors (National Instrument, USB-TC01) at the inlet. In an update compared to the previous work [Mona Shrestha et al., 2013], this version of the flow tube reactor was housed in an external temperature-controlled, double-hulled, water-jacketed housing that contained both the flow tube and the associated gas flow system. The resulting temperature was 20.0 ± 0.1 °C during each individual experiment (12-24 hr) and proved critical for reproducing experimental results of particle number-diameter distributions (i.e., tied to new particle production). The total pressure inside the flow tube, measured using a barometer (Omega PX409), ranged from 1.00 to 1.01 atm.
An air flow of 3.0 sLpm from an Aadco 737 Pure Air Generator passed through an ozone generator (Jelight, Model 600), producing 12 to 30 ppm of ozone. A syringe injector (CHEMYX, Fusion Touch 200 Model) provided (+)-α-pinene (Sigma-Aldrich, ≥ 99% purity, 97% enantiomeric excess) and 2-butoanol (Sigma-Aldrich, ≥ 99.5% purity; used as OH scavenger) at a dilution ratio of 1:49. The solution from the injector was introduced into the flow tube with an additional flow of pure, dry air at 0.50 sLpm. The concentration of α-pinene in the total flow was adjusted by changing the syringe injection rate.

**Figure 4-2 A schematic representation of the experimental setup.** Part I is the particle generation system. It was switched between the atomizer and the flow tube reactor for different purposes. Part II is the control system for RH. It consists of humidifying and drying components. SOM particles were brought to a controlled RH by using a Nafton tube. They entered one or more flask that acted as a plenum to allow time for coagulation. The particles were subsequently dried by diffusion dryers and another Nafton tube. Part III is the setup for particle characterization. A DMA-APM-CPC setup measured the mobility-filtered number-mass distribution. An SMPS measured the number-diameter distribution.
The aerosol flow out of the flow tube was passed to an ozone diffusion scrubber before entering the RH control setup. The ozone scrubber has an ozone removal efficiency of over 90%, which prevents further SOM production after aerosol particles exited the flow tube, so that aerosol coagulation became dominant over condensation in the subsequent flasks.

The RH control system for the particles consisted of one Nafion RH conditioner, a variable size flask used as the plenum, two diffusion dryers, and another Nafion RH conditioner. The dry SOM particles entering the system were humidified first and then brought back to dry RH before subsequent analysis. [Bateman, Belassein, & Martin, 2013]

Exiting the RH control system, the aerosol flow was divided into two streams. The first stream was sampled by a Differential Mobility Analyzer (DMA; TSI model 3081) [Knutson & Whitby, 1975]. The DMA outflow consisted of a subpopulation of particles having a central electric mobility diameter. The central diameters of the different experiments are listed in Table 4-1. The DMA outflow was sampled by an APM (APM-3600, KANOMAX Inc.) [Ehara et al., 1996], and the particle number concentration in the APM outflow was measured by a CPC (TSI model 3022a) [Agarwal & Sem, 1980]. The APM voltage was scanned at fixed rotation speed to measure the number-mass distribution of the particle population [M. Kuwata & Kondo, 2009].

The second flow stream from the reactor outflow was sampled by a SMPS (TSI, model 3071A; CPC; TSI, model 3772) to characterize the number-diameter distribution of the produced particle population [Hoppel, 1978]. The DMA, APM, and SMPS were regularly calibrated using aerosol particles of polystyrene latex (PSL) or ammonium
sulfate, both of which were produced by nebulization (Model 3076, TSI Corporation) [George Biskos, Vons, Yurteri, & Schmidt-Ott, 2008].

An Aerodyne high-resolution time-of-flight Aerosol Mass Spectrometer (HR-ToF-AMS) was used to characterize the chemical composition of the DMA-selected particles [DeCarlo et al., 2006]. Particles having mobility diameters of 50, 90, 120, 130, and 140 nm were sampled by the AMS for <15% up to >90% RH. Interferences from gas-phase CO$_2$ were compensated by the approach of Collier and Zhang [Collier & Zhang, 2013]. Elemental ratios were determined using the method of Canagaratna et al. [Canagaratna et al., 2014].

### 4.2.2 Instrument Calibration

Instrument calibration was conducted in two steps, first for the spherical particles and second for non-spherical particles. In the first step, an atomizer (Model 3076, TSI Corporation) was used to produced PSL aerosols particles having mobility diameters of 46 ± 2, 70 ± 3, 81 ± 3, 92 ± 3, or 125 ± 3 nm from aqueous suspensions (0.05% v/v; Thermo Scientific). The suspensions were used within one year of receipt. The flow of quasi-monodisperse PSL particles was brought to dry RH (< 5%) through two silica-gel diffusion dryers before the particles were characterized by the instruments. In the second step, aerosol particles were atomized from PSL (0.05% v/v) and ammonium sulfate solutions (0.1% w/w), and particles having a central mobility diameter of 126.0 ± 0.1 nm were selected by a DMA. The error bar represents the standard deviation (2σ) of DMA selected central mobility diameters due to the fluctuation of the sheath flow. The diameter-resolved particles were brought to various elevated RHs (described in Section 2.2) and subsequently dried to < 5% RH.
For the second part, particles having a central mobility diameter of 126.0 nm selected by a DMA were atomized from PSL (0.05% v/v) and ammonium sulfate solutions (0.1% w/w). The diameter-resolved particles were brought to various elevated RHs and subsequently dried to < 5% RH.

4.2.3 Measurement of the Dynamic Shape Factor

The relationship between the mass $m_p$ of a particle and the APM voltage $\phi$ and angular velocity $\omega$ is expressed as follows:

$$m_p = \frac{4eq\phi}{\omega^2(L_2 + L_3)^2 \ln(L_2 / L_3)}$$  \hspace{1cm} (4-1)

Here, $q$ is the number of charges on the particle, $e$ is the value of an elementary charge, and $L_1$ and $L_2$ are respectively the inner and outer radius of the cylindrical channel of the APM. [Ehara et al., 1996; M. Kuwata & Kondo, 2009] The mass-equivalent diameter $d_{me}$ of the particle is calculated based on $m_p$, as follows:[M. Kuwata & Kondo, 2009; Zelenyuk, Cai, & Imre, 2006]

$$d_{me} = \left(\frac{6m_p}{\pi \rho}\right)^{1/3}$$  \hspace{1cm} (4-2)

for a particle material density $\rho$. Here $d_{me}$ is used to calculate the dynamic shape factor $\chi$ since we assumed the particle has no internal voids.

The dynamic shape factor $\chi$ is calculated as follows:[DeCarlo, Slowik, Worsnop, Davidovits, & Jimenez, 2004]

$$\chi = \kappa \frac{\delta C_C (d_{me})}{C_C (\delta d_{me})}$$  \hspace{1cm} (4-3)
Here, $\delta$ is the porosity factor, $C_c(d_{me})$ is the Cunningham slip correction factor, and $\kappa$ is the envelope shape factor. The term $C_c(d_{me})$ is calculated as follows:[Dahneke, 1973]

$$C_c(d_{me}) = 1 + \frac{2\lambda}{d_{me}} (1.142 + 0.558e^{-0.999d_{me}^{2\lambda}})$$ (4-4)

where $\lambda$ is the mean free path of air at 293 K ($6.64 \times 10^{-8}$ m). The envelope shape factor $\kappa$ is expressed as follows:[DeCarlo et al., 2004]

$$\kappa = \frac{1}{\delta} \frac{d_m C_c(\delta d_{me})}{d_{me} C_c(d_m)}$$ (4-5)

where $d_m$ is the electrical mobility diameter of the particles, as selected by the DMA. By combining Eqs. (3) and (5), the dynamic shape factor is expressed as follows [DeCarlo et al., 2004]:

$$\chi = \frac{d_m}{C_c(d_m)} \frac{C_c(d_{me})}{d_{me}} = \frac{d_m}{(6m_p/\pi \rho)^{1/3}} \frac{C_c\left((6m_p/\pi \rho)^{1/3}\right)}{C_c(d_m)}$$ (4-6)

The porosity factor is seen to cancel out. Terms $d_m$ and $m_p$ are the direct measurements of the DMA-APM system. The material density $\rho$ is taken as 1050, 1770, and 1200 kg m$^{-3}$ for PSL, ammonium sulfate, and $\alpha$-pinene SOM, respectively.[Mikinori Kuwata, Zorn, & Martin, 2011] A sensitivity analysis is presented in the Figure 4-10 concerning the influence of the value of $\rho_{SOM}$ on the obtained shape factor.
Examples of the number-mass distributions recorded in three replicate experiments are shown in Figure 4-3. The DMA was set to select only the large-diameter particles in the tail of number-diameter distribution of the particle population. The selected particle subpopulation had a central mobility diameter of 126.0 nm compared to a mode diameter of 52.0 nm in the original population, which had 0.1 and 99.9% size intervals of 20.2 and 151.2 nm, respectively. Contributions from monomers, as well as from dimers of disparate monomer sizes (e.g., one large + one small) and other higher-order agglomerates, were therefore absent in the analyzed data sets. Although doubly
charged particles were present in the outflow of the DMA, the mass range covered in Figure 2 corresponds only to singly charged particles.

As a result of these filtering strategies, the subpopulation represented in Figure 2 consisted of singly charged dimer, trimer, and higher-order agglomerates. By use of Eq. (4-6), the dynamic shape factor of particles at the central value of the number-mass distribution was 1.18. Examples of the intrinsic width of the DMA-APM instrument train are denoted by the three dashed curves. The data are seen to be wider than the instrumental width. The subpopulation, therefore, consisted of particles having a quasi-monodisperse mobility diameter yet a range of dynamic shape factors, corresponding to a variety of different types of coagulated aspherical particles. Vertical lines are shown for $\chi$ values at 1.10 and 1.29, in addition to the central value of 1.18 as well as a reference value of 1.0. Cartoon representations of some examples of the types of particles that may be associated with the shape factors are represented as insets in the figure.

### 4.2.4 Modeling the Shape Change of Non-spherical Particles

To further understand changes in particle shape during coagulation, a COMSOL model was built to simulate the merging of non-spherical and suspended aerosol particles. The dynamic shape factors of the dry aerosol particles (<6% RH) were measured to be $1.18 \pm 0.02$ at 700 ppb $\alpha$-pinene, 12 ppm ozone concentration, and $1.26 \pm 0.02$ at 400 ppb $\alpha$-pinene, 15 ppm ozone concentration, respectively. The shape of the aerosols used in the COMSOL model is based on the literature data available. However, literature data showed that relationship between the actual geometric shapes of the aerosols and their dynamic shape factors is complicated and affected by several factors such as the intensity of the electrical field, the Knudsen number of the aerosol particle, the size range of the
aerosol particle as well as the orientation of the particle in the electrical field, etc. [Hansson & Ahlberg, 1985; Kousaka, Endo, Ichitsubo, & Alonso, 1996; Zelenyuk et al., 2006] The difference of dynamic shape factors of a parallel oriented particle versus a perpendicular oriented particle can be as large as 0.1. [Horvath, 1974; Kousaka et al., 1996] and the difference between difference literature results on the same particle shape can be as large as 0.06-0.16. [Hansson & Ahlberg, 1985] Hence the literature data are used as a reference. The reported dynamic shape values for doublets and triplets that are

**Figure 4-4** SEM images of the particles obtained from 700 ppb α-pinene and sampled for a central mobility diameter of 180.0 nm. The aerosol particles were collected on the silica substrate for 12 hr and then coated with 5 nm of Pt/Pd. The voltage for the electron beam was 5 kV, and the working distance was 2.3 mm. Column 1 shows dimer, trimer, and higher-order agglomerates of the granular monomers for <5% RH. Red circles identify the monomers. Column 2 shows nearly spherical particles that were collected after exposure to 80% RH followed by drying to <5% RH.

in 200-300 nm range were in between 1.036-1.16 and 1.116-1.28. [Hansson & Ahlberg, 1985; Hochrainer & Hanel, 1975; Kousaka et al., 1996; Zelenyuk et al., 2006] respectively. Considering the dynamic shape factors having a negative relationship with
particle mobility diameters, the shape factors for the particles measured in this study can be higher than the values reported in the literature. Here in this study the SEM images of the aerosol particles at dry conditions were also recorded, shown in Figure 4-4. The aerosol particles had the shape in between dimers and elliptical. Considering both the SEM images and the literature values, we used the upper limit of each study to characterize the geometric shape of the aerosols measured. The aerosol particles from the condition of 700 ppb and 400 ppb α-pinene were assumed to be doublets and triplets in the COMSOL models, respectively.

Each aerosol particle in the model has a diameter of 90 nm and overlaps with the other by 5 nm. The model was run at low, mid and high surface tensions based on the properties of 83 organic compounds and water [Korosi & Kovats, 1981]. The lower and medium surface tension values are based on the organic compounds, ranging from $2.0 \times 10^{-2}$ and $4.0 \times 10^{-2}$ N m$^{-1}$. The high surface tension is that of the water ($7.2 \times 10^{-2}$ N m$^{-1}$), assuming SOM is dissolved. For each run, the viscosity, longest and shortest axes of the particle were recorded at a designated time, which is the residence time of the SOM particles in the flask.

4.3 Results and Discussion

4.3.1 Calibration Result
The calibration of the DMA-APM setup was checked by selecting PSL particles with the DMA and using Eq. (6) to obtain $\chi$, as shown in Figure 4-5. That is, in Eq. (6) terms $\rho, m_p, \text{and } d_m$ were known for DMA-selected spherical PSL particles. The mass $m_p$ was obtained for the instrument settings via Eq. (1). By using effective density $\rho_{\text{eff}}$ in Eq. (6), the mass equivalent diameter $d_m$ can be cancelled out so that the uncertainty in shape factor estimation can be improved [M. Kuwata & Kondo, 2009]. An example of the number-mass distribution is shown in Figure 4-3. The peak of the distribution, which equals $m_p$, was calculated by fitting to a Gaussian function. Measurements were performed three times for each mobility diameters of PSL particles (46 ± 2, 70 ± 3, 81 ± 3, 92 ± 3, and 125 ± 3 nm). A calibration curve was made between the theoretical masses of PSL particles assuming they have a spherical shape and the real masses of the PSL particles.
particles measured. By using the calibration curve, the dynamic shape factor of PSL particles was determined to be within $1.00 \pm 0.01$ (two sigma). [Allen & Raabe, 1985]

The calibration shows that the uncertainty of the DMA-APM setup is $\pm 0.01$ (two sigma) for measurement of $\chi$. The shape factor for each mobility diameter is plotted in the Figure 4-6.

To calculate the shape factors for non-spherical particles and determine whether there is a dependence of shape factor on RH, similar measurements on both the PSL and ammonium sulfate particles ($d_m=126.0 \text{ nm}$) were performed. The calculation procedures were identical to the PSL particles and the experiments were repeated three times for each measured RH, shown in Figure 4-6. As shown in Figure 4-6, the shape factors of ammonium sulfate particles had values that were larger than those of the PSL particles. This difference is statistically significant, verified by the Student t-test method. This
result is consistent with the results from hygroscopic growth measurement [G. Biskos, Paulsen, Russell, Buseck, & Martin, 2006] and TEM images,[J. Li, Pósfai, Hobbs, & Buseck, 2003] which showed ammonium sulfate particles to have a shape factor of 1.02 and to be non-spherical. The data also suggest that exposing the PSL particles to different RHs did not seem to affect the shape factors within the error range, as consistent with the hydrophobic nature of PSL particles. However, the shape factors of ammonium sulfate particles were found to decrease at about 30% relatively humidity before it started to increase again. Since this RH is around the efflorescence RH of ammonium sulfate, this dependence plausibly arises from the shape change during the deliquescence and re-crystallization process when exposing the particles to a higher RH and then dried to < 5% RH. These calibration results show that the DMA-APM system can be used to determine properties of collections of suspended particles for a margin of error of 1% in the shape factor. The experiments with ammonium sulfate demonstrate that the system is appropriate for measuring non-spherical aerosol particles and characterizing the shape factors.

4.3.2 Dynamic Shape Factor of Non-spherical Particles at Fixed Relative Humidity

SOM particles were generated from the flow tube with 500, 700, and 1000 ppb of (+)-α-pinene at 12-13 ppm of ozone. The number concentrations and mode diameters of SOM particles are listed in Table 4-1. The RH was set to less than 6% for the SOM particles. A DMA was used to select mobility diameters of 70, 90, 120, 130 and 140 nm for the condition of 500 ppb, and 52.4, 60.0, 74.0, 85.6, 93.5, and 126.0 nm for conditions of 700 ppb. For the condition of 1000 ppb, DMA was used to select SOM particles
Table 4-3. Summary of experimental conditions.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Flow Tube SOM Generation</th>
<th>Precursor Conditions&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Particle Conditions&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Relative Humidity&lt;sup&gt;c&lt;/sup&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>α-Pinene (ppb)</td>
<td>Ozone (ppb)</td>
<td>Number Conc. (m&lt;sup&gt;-3&lt;/sup&gt;)</td>
</tr>
<tr>
<td>#1 Mid Concentration</td>
<td>700 ± 7</td>
<td>14.0 ± 0.2</td>
<td>(2.9 ± 0.2) × 10&lt;sup&gt;11&lt;/sup&gt;</td>
<td>63 ± 3</td>
</tr>
<tr>
<td>#2 Mid Concentration</td>
<td>700 ± 7</td>
<td>13.8 ± 0.2</td>
<td>(2.9 ± 0.2) × 10&lt;sup&gt;11&lt;/sup&gt;</td>
<td>66 ± 3</td>
</tr>
<tr>
<td>#3 Mid Concentration</td>
<td>700 ± 7</td>
<td>24.6 ± 0.8</td>
<td>(5.4 ± 0.3) × 10&lt;sup&gt;11&lt;/sup&gt;</td>
<td>80 ± 3</td>
</tr>
<tr>
<td>#4 Mid Concentration</td>
<td>700 ± 7</td>
<td>30.3 ± 0.5</td>
<td>(4.8 ± 0.4) × 10&lt;sup&gt;11&lt;/sup&gt;</td>
<td>80 ± 6</td>
</tr>
<tr>
<td>#5 High Concentration</td>
<td>1000 ± 10</td>
<td>13.0 ± 0.2</td>
<td>(4.3 ± 0.2) × 10&lt;sup&gt;11&lt;/sup&gt;</td>
<td>111 ± 2</td>
</tr>
<tr>
<td>#6 AMS Experiment</td>
<td>500 ± 5</td>
<td>13.0 ± 0.2</td>
<td>(2.6 ± 0.2) × 10&lt;sup&gt;11&lt;/sup&gt;</td>
<td>68 ± 3</td>
</tr>
<tr>
<td>#7 Mid Concentration</td>
<td>700 ± 7</td>
<td>14.8 ± 0.2</td>
<td>(3.4 ± 0.3) × 10&lt;sup&gt;11&lt;/sup&gt;</td>
<td>85 ± 3</td>
</tr>
</tbody>
</table>

<sup>a</sup>Concentrations at inlet of flow tube reactor. <sup>b</sup>Concentrations in the outflow of the reactor, as measured by SMPS. <sup>c</sup>Range of relative humidities studied in stepwise fashion in series of experiments. The overall RH cycle was (<5% RH) → (RH value from within range shown in table) → (<5% RH). Uncertainties correspond to one sigma. <sup>d</sup>For 100% RH, a flask with water was slightly heated until condensation was apparent on the walls.
having mobility diameters of 100, 126, 140, 150, 160, 170, 180 and 195 nm. The diameters chosen here are larger as the concentration of the α-pinene increases, mainly because the SOM particles generated from a higher concentration of α-pinene have a larger mode diameter and diameter distribution than the SOM from lower precursor concentrations. For a material density of $1.2 \times 10^3$ kg m$^{-3}$ for the SOM,[Mikinori Kuwata et al., 2011; McMurry, Wang, Park, & Ehara, 2002] the SOM particle shape factors under these three conditions and various mobility diameters were calculated and plotted in Figures 3.

As mentioned above, the shape factor of spherical particles is 1.00. As the shape factor increases, the particle deviates increasingly away from a spherical shape [DeCarlo et al., 2004]. The shape factors of SOMs generated from 500, 700, and 1000 ppb of (+)-α-pinene at mobility diameters larger than 70 nm were all above 1.00, and a positive correlation between diameter and shape factor at dry RH was observed, as illustrated in Figure 3.

The data are categorized based on the initial α-pinene concentrations in Figure 4-7. Although the particles all had shape factors that were larger than 1.00, the extent was different: experiments using 700 ppb of (+)-α-pinene were associated with the strongest positive correlation factor of shape factor with diameter whereas those using 500 and 1000 ppb of (+)-α-pinene condition were associated with weaker correlation factors. Firstly, the correlation suggests that particle number concentration affects the particle shape because coagulation depends on concentration. This observation can be explained as follows: the 500 ppb (+)-α-pinene concentration generated a lower particle
number concentration (and hence lower coagulation) than the 700 ppb (+) α-pinene concentration. With less coagulation, the dumbbell-shaped particles that formed through the collision of particles were not dominant, which makes the shape factor close to 1.00. Secondly, this correlation also suggests that particle coagulation frequency affects the scale of the shape factor too. For instance, for conditions of 1000 ppb (+)-α-pinene, although the particle number concentration was higher than that of the 700 ppb pinene condition, the particle shape factors were found to be smaller. By using the mode diameter and total number concentration, the lower estimated of the collision frequencies between 1000 and 700 ppb pinene SOM are $6.0 \times 10^{-4}$ s$^{-1}$ and $5.5 \times 10^{-4}$ s$^{-1}$, respectively. Although coagulation occurred more frequently at 1000 ppb pinene as opposed to 700 ppb pinene, the collision frequency ($6.0 \times 10^{-4}$ s$^{-1}$, estimated based on Seinfeld and Pandis)[Seinfeld & Pandis, 2006c] might have been too numerous to form the dumbbell-shaped particles.[Seinfeld & Pandis, 2006c] Instead, each particle might have undergone

![Figure 4-7 Examples of dynamic shape factors obtained for particle populations produced at different precursor concentrations (14 ppm ozone).](image)

- 500 ppb
- 700 ppb
- 1000 ppb
more than two collisions and became polyhedral shape, with a correspondingly lower shape factor, as illustrated in Figure 4-7.

Based on the above discussion, finding the right concentrations for the precursors is crucial for measuring shape factors using the DMA-APM system. The 700 ppb α-pinene concentration was used as the optimal concentration for generating non-spherical particles in this set of experiments (Figure 4-1). The optimal amount of coagulation was achieved by using flaks with combined volumes of 6.6-7.5 L after the Nafion RH conditioner to somewhat enhance the coagulation, but a medium concentration of precursor was injected so that the collision rate between particles would not get too high. At the same time, the wall effects (particle diffusion and wall loss) of the flask also affected the final particle number-diameter distribution and the shape factor results.

**Aerosol mass spectrometer (AMS) measurement of O:C and H:C ratios**

![Graph](image)

*Figure 4-8 Diameter-resolved O:C and H:C elemental ratios obtained by AMS for sampling of the particle population produced from 500 ppb α-pinene and 14 ± 1 ppm ozone. The red and blue data sets represent measurements for low (<15%) and high RH (>90%) exposures, respectively. In both cases, the RH was reduced to <5% RH prior to measurement.*
The goal of the AMS measurement under condition of 500 ppb was to test whether particle material density depended on diameter and verify the hypothesis that the density for SOM particles at different diameters was the same \((1.20 \times 10^3 \text{ kg m}^{-3})\). Since a constant material density was used for calculating the dynamic shape factor, a change of the material density will affect the value of the shape factor. The O:C and H:C results from the measured particles were averaged according to different diameters and are plotted in Figure 4-8, and the results agree well with the previous measurement of similar mass loading [Qi Chen, Liu, Donahue, Shilling, & Martin, 2011]. The diameter independence of the results for the O:C and H:C elemental ratios, implies that the material density also did not depend on diameter. If the result had been otherwise, the data analysis for the dynamic shape factor would have become more complicated. The O:C and H:C ratios did not depend strongly on particle diameter, which implies that the particle composition/density did not have a strong dependence on diameter. Hence, the fundamental reasons for shape factor variation between particles diameters are physical property changes rather than chemical ones. The results plotted in Figure 4-8 also show that the O:C and H:C elemental ratios did not depend on RH. If the result had been otherwise, the inference would have been that chemical reactions occur with increasing RH, which would have complicated the scientific interpretation of the RH dependence of viscosity.

4.3.3 The Dynamic Shape Factor and Particle Merging at Increased Relative Humidity

Section 4.3.1 summarized that the changes in particle shape for certain diameters at various α-pinene conditions and that the change was possibly due to two colliding
particles merging into one single large non-spherical particle. This non-spherical shape indicates that the viscosity of the particle was too high to prevent it from forming a sphere to minimize the surface tension. Previous publications have shown that the viscosity of water soluble parts of α-pinene SOM has a strong dependence on RH [T. Koop, J. Bookhold, M. Shiraiwa, & U. Poschl, 2011; Renbaum-Wolff et al., 2013f]. Thus, a lower viscosity at a higher RH may drive the particles into round shapes.

**Long exposure to RH controlled flask**

In this part of the study, all the aerosol particles were exposed to the RH controlled flask with a volume of 6.6 L, which is equal to 310 seconds of residence time.

**Figure 4-9 Full data set of dynamic shape factors measured in the present study for exposure to elevated RH for 310 s.** Corresponding α-pinene and ozone concentrations were 700 ppb and 14 ± 1 ppm. The error bars represent two sigma.

Since the change in particle shape was largest for the ozonolysis of 700 ppb (+) α-pinene, this study focuses on this pinene concentration as an example of data analysis. The RH was varied between 3 to 95% for all the particles measured (Figure 4-7) and the ozone concentration was 14 ppm. The shape factors of SOM particles having diameters
of 52.4, 74.0, 85.6, and 93.5 nm did not depend strongly on RH, with all shape factors less than 1.02. Random fluctuations in the shape factors were observed, which was attributed either to measurement error or an insignificant change in particle shape. For instance, particles with 93.5 nm diameter exhibited a slight increase in shape factor at both low RH and high RH levels. At low RH, the observed shape change might be due to weak coagulation between particles of similar diameters. At high RH, the shape change may be attributable to trace absorbent water adhering to the particle surface after bringing SOM particles to high RH and then drying them down to less than 5% RH.

For 126.0 nm mobility diameter particles, the measurements were repeated twice, once the RH was scanning up and for the second one the RH was scanning down, both of which the shape factor changed significantly. At 3% RH, the shape factor was found to be $1.21 \pm 0.02$, which is $5-10$ times more than the shape change of particles at other diameters. As the RH increased, the shape factor of the particles was found to gradually decrease and finally reached a constant value at 35% RH. The change in particle shape implies a decreasing viscosity when particles were exposed to an increasing RH environment. The finding that particles became round at 35% RH also agrees well with the reported results$^4$ that the viscosity of $\alpha$-pinene-derived SOM at this RH lies between the solid and the semi-solid range. A COMSOL model was built to quantitatively estimate the upper and lower limits of the viscosity between 3 to 35 % RHs, which is described in Section 3.6.
A sensitivity analysis was conducted to test the effects of assumed material density on shape factor for the above condition. Particle shape factors calculated from different material density were plotted in Figure 4-10. Although the absolute value of shape factors changed about 10% as material density changed 5%, the relative different among shape factors remained to be the same. Moreover, the analysis suggests that the material density of $1.2 \times 10^3 \text{ kg m}^{-3}$ is the correct value for this study since the this value is the gives a shape factor closest to 1.00 among all other densities when exposed to high RH.

![Figure 4-10 Sensitivity analysis of the effect of the uncertainty in material density on calculated shape factors (Eq. 4-6). Five values of material density are used to calculate the shape factors from the same data set of $d_m$ and $m_p$ (viz. for experiments of 700 ppb of $\alpha$-pinene and 14 ppm ozone). The dashed line represents a reference point for a shape factor of 1.00, corresponding to a spherical particle.](image-url)
To verify the results at other conditions, the ozone concentration was raised to 25 and 30 ppm, where the particle number diameter distribution also shifted toward high diameters due to an increasing SOM production. Mobility diameters of 175.0 and 195.0 nm were selected for the measurements in these two conditions, respectively. The results showed similar trends and were plotted in Figure 4-11.

**Figure 4-11 Dynamic shape factor for increasing RH.** Particles produced from 700 ppb α-pinene and 14, 25, and 30 ppm ozone for particle populations having central mobility diameters of 126.0, 175.0, and 190.0 nm, respectively. The exposure time to RH was 310 s.

**Short exposure to RH controlled flask**

Since non-spherical SOM particles could reform themselves towards round particles as RH increased, the time of exposure also affects the extent of the reforming process and hence the shape factors. For the above experiments, the residence time of the aerosols in the RH controlled environment was 310 s. In the experiments of this section, the 6.6 L flask was used as a coagulation plenum and then connected to a smaller flask.
(0.9 L) which is used as the RH controlled flask, so that the exposure time of SOM particles to high relative humidities particles can be decreased to 45 s. With a shorter exposure time, the same shape change under the 310 s residence time would need a higher RH to complete. Hence, the whole shape factor versus RH curve would be expected to shift towards the right.

The $\alpha$-pinene concentration was set to 400 ppb and ozone concentration was 15 ppm. Since the ozone concentration was higher and the coagulation time is longer in this experiment compared to the previous experiment, the concentration of $\alpha$-pinene required to achieve maximum dynamic shape factor could be as low as 400 ppb. A mobility diameter of 165.0 nm is selected and the RH was increased from 4% to 58%.

![Figure 4-12 Dynamic shape factor for increasing RH (short residence time).](image)

Figure 4-12 Dynamic shape factor for increasing RH (short residence time). Exposure up to 80% RH for 45 s or 310 s. SOM was produced from 700 ppb $\alpha$-pinene and 14 ppm ozone at <5% RH. The error bars in each panel represent two sigma of standard deviation.
during the experiment. The dynamic shape factors of this condition were plotted against RH in Figure 4-12. As a comparison, the data from the condition of 700 ppb is also plotted in Figure 4-12.

The results support the hypothesis. The dynamic shape factor of the SOM particles had an average of $1.26 \pm 0.02$ at 4-16% RH, and then started to decrease at 20% RH. At about 60-65% RH, the dynamic shape factor seemed to reach a stable value and was close 1.00, which suggests that the particles were round at this RH and beyond. The curve of dynamic shape factor versus RH from the condition of 45 seconds residence time shifted for about 20% RH compared with the results from the condition of 310 seconds residence time.

The results support the hypothesis. The dynamic shape factor of the SOM particles had an average of $1.26 \pm 0.02$ at 4-16% RH, and then started to decrease at 20% RH. At about 60-65% RH, the dynamic shape factor seemed to reach a stable value and was close 1.00, which suggests that the particles were round at this RH and beyond. The curve of dynamic shape factor versus RH from the condition of 45 seconds residence time shifted for about 20% RH compared with the results from the condition of 310 seconds residence time.

4.3.4 Viscosity Estimation

The viscosity of the SOM particles can be determined by the following procedures. Firstly, SOM particles were exposed to different levels of relative humidities under two residence times (45 s and 310 s), by using a 6.6 liter flask and 0.9 liter flask. Based on the DMA-APM results, the measured particle dynamic shape factors $\chi$, are
plotted against relative humidities $RH$, in Figure 6. The relationship follows Hill equation (Figure 6), which can be expressed as:

$$\chi = f_i(RH) = a_i + (b_i - a_i) / \left[ 1 + \left( \frac{c_i}{RH + e_i} \right)^{d_i} \right]$$

(4-7)

where $a_1$, $b_1$, $c_1$, $d_1$, $e_1$ are all fitting coefficients

Secondly, by using the COMSOL model, particle shape information can be obtained at these two residence times. An example of the model simulation is shown in Figure 4-13 Flow simulation for the transformation of a dimer agglomerate into a spherical particle. Panel A shows the initialization for $t = 0$ s. Two monomers having a diameter of 45 nm and overlapping by 5 nm are shown. The coloring represents the instantaneous flow velocity. Panel B shows the end of the simulation at $t = 310$ s. The full time series is shown in SI Movie S1. The viscosity and its standard deviation, $(1.0 \pm 0.2) \times 10^8$ Pa s, were optimized in the simulation so that the transformation from a dimer in Panel A to a sphere in Panel B was complete after 310 s. In panel B, the black lines represent the original shape of the particle (i.e., panel A).
Figure 4-13. A dimer consisting of two 90-nm diameter spheres having an overlap of 5 nm between the spheres was modeled for an exposure of 310 s to elevated RH. Here, geometry was described by the longest axis $L_1$ and the shortest axis $L_2$. A geometry factor $\xi$, defined as $\xi = (L_1/L_2)^2$, was used to quantify particle asphericity. The rationale for defining $\xi$ is that $L_1^2$ and $L_2^2$ are proportional to the maximum and the minimum cross-sectional areas of the particle, respectively, and the drag force scales with cross-sectional areas. The ratio therefore is a metric of the aerodynamic deviation of the particle from a sphere. For a value of unity, $\xi$ describes a sphere. The geometry progressively deviates from spherical for larger $\xi$. The upper limit of $\xi$ is four or nine for the tangential limits of dimer and trimer geometries, respectively.

For a trial value of viscosity, the model was allowed to evolve for 310 s (dimer case; I) or 45 s (trimer case; II). At the end of the simulation time, the geometry had evolved because of material flow. For this geometry, an updated value $\xi_f$ was calculated. The subscript $f$ denotes the final geometry. This process was repeated for a full range of viscosity values.

The curves of $\eta(\xi_f;X)$ for the two base cases were empirically fit, as follows:

$$\eta(\xi_f;X) = \left( \frac{b + a}{\xi_f + a} \right)^d c + e$$  \hspace{1cm} (4-8)

for fitting coefficients $a$ through $e$.

there is a monotonic relationship between the geometry factor $\xi(X)$ and the aerodynamic dynamic shape factor $\chi(X)$. In implementation, only the endpoints were constraint, and a linear relationship between them was assumed, as follows:
Viscosity and Merging of Suspended Particles

\[
\xi(X, \chi) = m\chi + q
\]  
(4-9)

for fitting coefficients \( m \) and \( q \).

Combining Eqs. (4-7)-(4-9) leads to the following result:

\[
\eta(X, \chi) = \left( \frac{b + a}{m\chi + q + a} \right)^\varphi c + e
\]  
(4-10)

The shape factors \( \chi_{f,X} \) were the final values after exposure to an elevated RH. Solving this function will generate a relationship between viscosity and RH, as shown in Figure 4-14.

**Figure 4-14 Summary of the RH-dependent viscosity obtained from this study for \( \alpha \)-pinene SOM for <5% RH to 58% RH.** The secondary y axis shows the mixing time of low volatility molecules with an 100-nm particle. Part I represents data for changes in the shape factor for residence time of 310 s. Part II represents data for 45 s. The secondary y axis shows the characteristic mixing time \( \tau \) of low volatility organics due to bulk diffusion in 100-nm particles of the same viscosity. Results from literature are also plotted for comparison. A breakdown of the factors contributing to the uncertainty bars is presented in Figure A-2

Based on the model simulation, the viscosity values can be determined from 3% all the way to 65% for \( \alpha \)-pinene derived SOM. At 3% RH and 65% RH were estimated
as \((1.0 \pm 0.5) \times 10^9\) Pa s and \((3.9 \pm 2.5) \times 10^7\) Pa s, respectively. The estimated viscosity from the condition of \(<5\%\) RH is within the upper limit of Abramson et al.\(\text{[Abramson et al., 2013]}\) by estimating the diffusivity through the evaporation of pyrene in SOM under dry condition. And the estimated viscosity values are in between the results from Abramson et al. and Pajunoja et al. But, the values are smaller than the values reported by Renbaum-Wolff et al. at low RH and is higher than those reported by Renbaum-Wolff et al at higher RH,\(\text{[Renbaum-Wolff et al., 2013f]}\) which is plausibly due to the composition difference (i.e. the study above measured the viscosity of total SOM rather than the water soluble part). Moreover, the DMA-APM technique also estimates viscosity continuous during the selected RH range rather than providing discrete data points.\(\text{[Kidd et al., 2014a; Renbaum-Wolff et al., 2013f]}\) This method provides a new way to estimate and compare particle viscosity.

The Stokes Einstein Equation, which describes the relationship between diffusion coefficient of organic compounds in the particle \(D_{\text{org}}\) and viscosity \(\eta\),\(\text{[Shiraiwa, Ammann, Koop, & Pöschl, 2011a]}\) can be expressed as:

\[
D_{\text{org}} = \frac{kT}{6\pi r_g \eta}
\]  \(\text{(4-11)}\)

where \(k\) is the Boltzmann constant \((1.38 \times 10^{-23}\) J K\(^{-1}\)), \(T\) is the absolute temperature, \(r_g\) is the effective molecule radius of the gas phase species and \(\eta\) is the dynamic viscosity.

The characteristic time \(\tau_p\) to achieve equilibrium (i.e. the mixing time) in the gas-particle interface\(\text{[Seinfeld & Pandis, 2006c]}\) can be expressed as:

\[
\tau_p = \frac{d_p^2}{4\pi^2 D_{\text{org}}}
\]  \(\text{(4-12)}\)
Assuming the diameter of the particle $1 \times 10^{-7}$ m, the radius of the gas phase molecule $r_g$ is $3.8 \times 10^{-10}$ m [Renbaum-Wolff et al., 2013f] and a room temperature $T$ is 293 K, by using Eq. (7) and Eq. (8), the diffusion efficient and the mixing time are calculated and listed in Table 4-2.

The diffusion coefficients at RH conditions of 3% and 65% were then inferred via the Stokes-Einstein equation, which are $5.6^{+5.7}_{-1.8} \times 10^{-22}$ and $1.4^{+2.6}_{-0.5} \times 10^{-20} \text{ m}^2 \text{ s}^{-1}$. The results indicate that SOM particles do not reach instant equilibrium with the gas phase when the RH is between 3-65%. For the RH conditions of 3%, the characteristic equilibrium time is about five to six days, which supports the results of recent studies that current models can overestimate SOM particle mass and underestimate gas-phase concentration by more than an order of magnitude by assuming instant equilibrium of gas phase species in the particle phase [Perraud et al., 2012; Riipinen et al., 2011] Estimating the viscosity values at low RHs from this technique could, therefore, help give a more precise estimate of SOM mass production, thereby improving the accuracy of air quality and climate models. The characteristic equilibrium time of RH between 65% is on the

<table>
<thead>
<tr>
<th>Relative Humidity (%)</th>
<th>Viscosity ($\text{Pa s}$)</th>
<th>Characteristic Mixing Time (day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;5</td>
<td>$10^{(8.7 \pm 2.0)}$</td>
<td>$10^{1.0 \pm 2.0}$ (11.5 days)</td>
</tr>
<tr>
<td>58</td>
<td>$10^{(7.0 \pm 2.0)}$</td>
<td>$10^{-0.68 \pm 2.0}$ (5.0 hr)</td>
</tr>
</tbody>
</table>

Also shown are the characteristic mixing times for a diffusing species in a spherical SOM particle of 100 nm. An effective radius of 1.5 nm is used. See main text for further explanation.
order of a few hours. Small gas phase molecules can penetrate into the particles and reach equilibrium while large molecules may be confined at the outer layers of the particles.

4.4 Conclusions

In summary, the DMA-APM system successfully measured the particle shape factor of α-pinene SOMs over a range of RH. Mass spectra recorded for the particles suggested that no change in chemical composition occurred with the change in shape factor, providing evidence against any possible water-driven chemical reactions as the explanation that could drive changes in particle shape. Particle viscosity was estimated continuously from \((1.0 \pm 0.5) \times 10^9\) Pa s at 6% RH down to \((3.9 \pm 2.5) \times 10^7\) Pa s at 65% RH by using the COMSOL model.

These results can improve the estimate of reactive uptake of gas species into particles and help model the subsequent oxidization processes. Small molecules, such O\(_3\) or NO\(_x\), can diffuse into particles and react with particle-phase components. The depth and speed of the reactions are largely dependent on the diffusion coefficient of the particle components, which can be inferred from the viscosity coefficient. This study may therefore aid the understanding of aerosol particle aging under low RH conditions.

Moreover, this methodology can measure the particle property in situ, rather than being collected on a substrate for sequent analysis, which can provide particle shape and viscosity information without extracting the components and transferring the SOM particles to any medium. Therefore, the estimate of SOM viscosity based on this study provides a new way of estimating viscosity of the aerosol particle by using the COMSOL model.[Renbaum-Wolff et al., 2013f] The experiments here provided the viscosity of α-pinene derived particle 3-65% RH at a temperature of 20 °C, while further studies of
particle viscosities at higher RH levels and other temperatures are being conducted by using the above method. The viscosity of SOM generated from other VOCs also needs to be further investigated.
5. Effects of Water on the Secondary Organic Material

5.1 Introduction

The propensity of atmospheric organic particles to undergo growth and participate in chemical reactions is influenced by the ambient RH [Hallquist, Wenger, Baltensperger, Rudich, Simpson, Claeys, Dommen, Donahue, George, Goldstein, Hamilton, Herrmann, Hoffmann, Inumia, Jang, Jenkin, Jimenez, Kiendler-Scharr, Maenhaut, McFiggans, Mentel, Monod, Prevot, et al., 2009; Kidd, Perraud, Wingen, & Finlayson-Pitts, 2014e; Renbaum-Wolff et al., 2013a]. Recent research has shown that SOM changes from highly viscous, or glassy, at low RH or low temperatures to low viscosity at high RH [Thomas Koop, Johannes Bookhold, Manabu Shiraiwa, & Ulrich Poschl, 2011c; Renbaum-Wolff et al., 2013a; Saukko et al., 2012]. In other words, the SOM is "rock-like" under low RH, "honey-like" under intermediate RH, and "liquid-like" under high RH. Given the importance of SOA particles in the climate system [Chan et al., 2010; Claeys et al., 2004; C. J. Ebben, M. Shrestha, I. S. Martinez, A. L. Corrigan, A. A. Frossard, W. W. Song, D. R. Worton, T. Petäjä, et al., 2012; Y. Gao, Hall IV, & Johnston, 2010d; Hallquist, Wenger, Baltensperger, Rudich, Simpson, Claeys, Dommen, Donahue, George, Goldstein, Hamilton, Herrmann, Hoffmann, Inumia, Jang, Jenkin, Jimenez, Kiendler-Scharr, Maenhaut, McFiggans, Mentel, Monod, Prevot, et al., 2009; Kroll & Seinfeld, 2008a; Lee & Kamens, 2005; Poschl, 2005; Michael P. Tolocka et al., 2006; Yu, Cocker, Griffin, Flagan, & Seinfeld, 1999; D. Zhang & Zhang, 2005], and the dynamic nature of RH in most environmental settings [B. Finlayson-Pitts & Pitts, 2000; Seinfeld & Pandis, 1998], the particle interactions with water vapor [Mikhailov, Vlasenko, Martin, Koop, &
Poschl, 2009] has important implications in the particle phase chemistry [Mikinori Kuwata & Martin, 2012], lifetime and transport of aerosol particles [Zhou, Shiraiwa, McWhinney, Poschl, & Abbatt, 2013] as well as the morphology[Adler et al., 2013] and optical properties [Adler, Haspel, Moise, & Rudich, 2014]. For instance, slow diffusion of the evaporating component within the particle bulk may lead to slow mixing within the particle imposing a kinetic limitation on the gas-particle heterogeneous reactions. SOM formed under high RH conditions may therefore become “inactive” to gas phase oxidants under low RH conditions due to the low diffusion coefficient of the gas phase compounds under high visocisty conditions. Until the RH rises again, the chemical composition of the particles remains static. Detailed kinetic models [Roldin et al., 2014; Shiraiwa, Zuend, Bertram, & Seinfeld, 2013; Zaveri, Easter, Shilling, & Seinfeld, 2014] are required to unravel the complexities of SOM processes, and these require knowledge of the diffusion coefficients of component species across the full range of atmospherically relevant RH and temperatures. Previously, measurements of water uptake and loss have been used to estimate water diffusion coefficients in single-component aqueous solutions [Lienhard et al., 2014; Zobrist et al., 2011]. However, direct measurements of water diffusion in SOM do not currently exist. To address this, laboratory measurements of the diffusion coefficient of water in α-pinene SOM are performed over a range of temperatures and RH conditions.

At the molecular level, RH also shows an impact on molecular orientation distributions. This impact could influence heterogeneous processes occurring at the particle surfaces and its bulk. When molecular orientation at the surface is more organized, these surface molecules are largely impenetrable to gas phase species, while a
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disordered array of surface species may permit more efficient surface accommodation and absorption into the bulk [Hopkins, McFearin, & Richmond, 2011; Moussa et al., 2009]. Currently no technique exists that can selectively probe the surfaces of suspended SOA particles under ambient conditions using molecular spectroscopy. Nevertheless, by applying vibrational SFG spectroscopy, the surface orientation information of SOM particles from Teflon filters can be obtained. SFG spectroscopy is a well-established surface analysis method for determining molecular orientation distributions of organic materials undergoing phase transitions [Sefler et al., 1995] or submersed in environments of varying dielectric constant [Wang, Woodcock, Buck, Chen, & Chen, 2001]. Shen and co-workers reported spectral intensity reductions in the methylene C–H stretching region upon freezing eicosane (C_{20}H_{42}) and attributed this observation to a reduction in gauche (–CH2–CH2–) defects [Sefler et al., 1995]. Likewise, Chen and coworkers reported SFG spectra from C–H oscillators on polymer side chains that identify changes in their molecular orientation as the polymer is placed in water vs. air [Wang et al., 2001]. Most recently, Richmond and coworkers [Robertson, Carpenter, Olson, Ciszewski, & Richmond, 2014] clearly showed increases in the SFG signal intensities from C–H stretches of a charged polymer as the extent of molecular order within the surface-localized polymer increased by addition of Ca^{2+} ions. In contrast to the bulk analysis measured above, the study in this thesis successfully measures nano-gram scale α-pinene-derived SOM [M. Shrestha, Y. Zhang, C. J. Ebben, S. T. Martin, & F. M. Geiger, 2013] and provides the first RH-dependent vibrational SFG spectra obtained from the surfaces of α-pinene-derived SOM deposited on optical windows.
To sum up, in this chapter, two aspects the effects of water on aerosol particles are studied. Firstly the diffusion rates of water vapor into the aerosol phase are measured across different temperatures. The results are then parameterized and used in a multilayer spherical diffusion model to simulate water uptake and loss under atmospheric conditions with varying updraft wind speeds. The collaboration study shows that water diffusion is not kinetically limited in 100 nm particles on atmospheric timescales at 280 K, but is slow enough to impact atmospheric processes at even lower temperatures. Second, the molecular structures and orientations of the particle surface are analyzed under different RH levels. The SFG spectra suggests more ordered and less ordered C–H oscillators under low and high RHs, respectively, to the external world. We find fully reversible changes in the SFG responses as we subject the SOM to approximately <5% to 95% RH and discuss the atmospheric implications of our findings in the context of the propensity of atmospheric organic particles to undergo particle growth, participate in chemical reactions, and CCN activity.

5.2 Experimental

5.2.1 Precipitator Sample Collection

Aerosol particles were prepared by ozonolysis of the volatile precursor (+)-α-pinene in a flow tube reactor [M. Shrestha et al., 2013]. α-pinene and ozone were injected into the Harvard flow tube reactor via two different inlets maintained at ambient temperature and pressure under conditions that lead to condensational growth. The flow tube was equipped with ozone (Ecosensors, UV-100) and temperature sensors (National Instrument, USB-TC01) at the inlet. The flow tube reactor was housed in an external temperature-controlled, double-hulled, water-jacketed housing that contained both the
flow tube and the associated gas flow system. The temperature was 20.0±0.1 °C during each experiment since accurate temperature control was critical for reproducing experimental results of particle number-diameter distributions. The total pressure inside the flow tube, measured using a barometer (Omega PX409), ranged from 1.00 to 1.01 atm. An air flow of 3.0 sLpm from an Aadco 737 Pure Air Generator passed through an ozone generator (Jelight, Model 600), producing 12 to 16 ppm of ozone. A syringe injector (CHEMYX, Fusion Touch 200 Model) provided (+)-α-pinene (Sigma-Aldrich, ≥ 99% purity, 97% enantiomeric excess) and 2-butanol (Sigma-Aldrich, ≥ 99.5% purity; used as OH scavenger) at a dilution ratio of 1:49. The solution from the injector was introduced into the flow tube with an additional flow of pure, dry air at 0.50 sLpm. The concentration of α-pinene in the total flow was set to be 700 ppb by adjusting the syringe injection rate. The particles were grown without seed particles and ranged in mode diameters from 35 to 150 nm, depending under what conditions they are prepared and collected.
The SOM aerosol particles in the outflow from the flow tube reactor were passed through a precipitator (TSI, 3077) and deposited uniformly on CaF$_2$ optical windows [Liu, Zhang, & Martin, 2013], which were used directly for the spectroscopic analyses. The precipitator consisted of a grounded cylindrical housing having a central electrode target (2.54 cm diameter). The collection voltage (<10 kV) of the precipitator was kept at 9.5 kV to collect particles. SOA particles charged by the neutralizer were deposited for 30 minutes to 2 hours onto the substrate with a flow rate of 2 liters per minute. The CaF$_2$ windows were cleaned in methanol and Millipore water, dried in an oven, placed in a plasma cleaner (Harrick Plasma) at Northwestern, and was placed in UV/ozone cleaner (Windsor Scientific, model ProCleaner-Plus) to avoid contamination with organic species deposited from lab air. The window was placed on the high voltage electrode of the collection conducted by the electrostatic precipitator.

**Figure 5-1 Electrostatic Precipitator and it’s components.**

5.2.2 Filter Sample Collection

The filter collection used the same outlet that was used for precipitator. Depending on the purpose of the experiment, either a Teflon filter or a quartz filter was
used. When ready, the filter was put on the filter sample holder and then screwed into the sample box for filter collection. The mass of the particles collected on the filter was estimated by using the following equation:

\[ m = f \eta c_{\text{mass}} \]  

Here, \( f \) is flow rate, \( t \) is collection time, \( \eta \) is collection efficiency and \( c_{\text{mass}} \) is the particle mass concentration obtained from a SMPS, assuming a particle density of 1200 kg m\(^{-3}\) and a collection efficiency near unity. The maximum mass for the Teflon samples was 0.2-0.5 mg of SOM, while for the quartz samples it was 10 mg of SOM.

For the diffusivity experiment, the concentration of \( \alpha \)-pinene in the total flow was set to 6 ppm by adjusting the syringe injection rate [Mona Shrestha et al., 2013]. The concentrations reported here are those at the inlet of the flow tube. The aerosol particles that flowed out of the flow tube were measured by a SMPS, given a mass concentration of 10 mg m\(^{-3}\). The particles were also collected onto a quartz filter for 48 to 63 hours. The SOM on the filter was then extracted by 5.00 mL of D.I. water through ultrasonication for 30 minutes and used for this experiment.

For the surface orientation experiment, the \( \alpha \)-pinene concentration was set to 125 ppb and the filter was collected for 83 hours. The collected filter was then pressed by hand against clean CaF\(_2\) optical windows to transfer SOM onto them, followed by the removal of the filter from the windows and subsequent analysis.
5.3 Results and Discussion

5.3.1 Comparison of Different Collection Techniques

Both filter collections and precipitator collections have their own advantages and disadvantages. In the case of filter collections, either a Teflon filter or a quartz filter is used. A Teflon filter has an upper collection limit of 0.2 mg and does not need pretreatment while a quartz filter can collect samples for a few mg but has to be heated at 800 °C for 12 hours to remove any adhesive VOCs. Compared the precipitators, filters can collect more mass but it is difficult to study the collected SOM mass on top of it because it has to be transferred to the optical substrate or dissolved into the solvent for further treatment. The transfer and the dissolution processes can result in a change in particle composition and increase the uncertainty for the analysis.

Precipitator samples, on the other hand, have much less SOM masses compared with filter samples. Nevertheless, the aerosol particles can be directly deposited onto the surface of a chosen substrate and directly analyzed using sensitive optical techniques. In conclusion, filter sampling is more suitable for large SOM mass analysis and those techniques involving re-dissolution where a pre-existing substrate is needed.

5.3.2 Influence of Water Activity on the Diffusivity of Secondary Organic Material

The sample collection was conducted at Harvard. The water diffusion experiment and the related analysis were primarily performed at University of Leeds by Hannah Price. Briefly, for each experiment, a single aliquot of the SOM solution was pipetted onto a hydrophobic glass slide and formed into a disk of ~200 μm radius and ~25 μm thickness by placing a second, smaller glass slide on top, with spacers on either side.
After equilibration in a temperature and humidity controlled cell to achieve a uniform water activity of RH/100, the H$_2$O vapor in the gas flow was replaced by D$_2$O vapor at the same dewpoint. D$_2$O diffusion into the disk was observed via a Raman microscope, and the spatial and temporal evolution of the O-D and O-H bands were used to quantify water diffusion coefficients (see SI text for details of the quantitative analysis of the SOM Raman spectra). Measurements were made between 240 and 280 K, over a water activity range of 0.15 to 0.8 and experiments were repeated over a period of time to verify that the diffusion coefficients were unaffected by sample age. Measurements at lower temperatures were not possible due to the required duration of the experiments (data for the slowest diffusion coefficients presented here took several weeks to obtain) and measurements at higher temperatures were affected by increase in sample fluorescence over the course of the experiment.

The measured diffusion coefficients by the University of Leeds are plotted vs. water activity and temperature in Fig. 5-2, with each data point representing a diffusion measurement on one disk. We report diffusion coefficients in terms of water activity, as
opposed to RH, to emphasize the importance of kinetics. It is the water activity of SOM which determines its diffusion coefficient, which is not necessarily the same as the surrounding RH/100. Unless a particle is in equilibrium with water vapor, its water activity, and hence diffusion properties, will be non-uniform. An empirical fit to the data was produced using a Vignes-type equation\cite{Lienhardetal2014,Mattiesenetal2011,Vignes1966}:

\[
D_{\text{water}} = (D_{\text{water}}^0)^{x_w\alpha} (D_{\text{SOM}}^0)^{1-x_w\alpha}
\]  

(5-2)

where \(D_{\text{water}}^0\) is the temperature-dependent self-diffusion coefficient of water\cite{RSM1999} and \(D_{\text{SOM}}^0\) is the diffusion coefficient of water in amorphous SOM at water activity, \(a_w = 0\). \(D_{\text{SOM}}^0\) is constrained to fit the form of a Vogel-Fulcher-Tammann (VFT) relationship \cite{Angell1995}:
\[
\log_{10}(D_{SOM}^0) = -\left( A + \frac{B}{T - T_0} \right)
\]

in which \( A \), \( B \) and \( T_0 \) are fitted parameters indicating the high temperature limit of the diffusion coefficient, the fragility and the temperature at which the diffusion coefficient would diverge, respectively. \( x_w \) is the mole fraction of water, calculated from the water activity using the effective hygroscopicity parameter (\( \kappa_{org} = 0.1 \)) [Thomas Koop et al., 2011c; Petters & Kreidenweis, 2007], and \( \alpha \) is an activity coefficient [Lienhard et al., 2014; McGlashan, 1963].

Figure 5-2 compares our measured water diffusion coefficients at 280 K with predictions of water diffusion coefficients in \( \alpha \)-pinene SOM based on the semi-empirical VFT-based approach developed by Berkemeier, Shiraiwa, Pöschl, and Koop (2014) also at 280 K. The predictions from this approach are lower than our experimental data, which could be due to differences between the composition of our SOM sample and the model SOM composition used by Berkemeier et al. (2014) in the semi-empirical VFT approach. The data with diffusion coefficients estimated from room temperature viscosity measurements made on \( \alpha \)-pinene SOM generated in a chamber [Renbaum-Wolff et al., 2013a] and in the flow tube [Y. Zhang et al., 2015] are also cross-compared. The Stokes-Einstein equation is here used to convert viscosities to diffusion coefficients, and leads to values that are up to 8 orders of magnitude smaller. These values are not surprising because the hydrodynamic Stokes-Einstein relation is known to break down at high viscosity and the diffusion coefficients of water and larger solute molecules generally deviate near the glass transition [Champion, Hervet, Blond, Le Meste, & Simatos, 1997; Power et al., 2013; Rampp, Buttersack, & Lüdemann, 2000; Zhu et al., 2011]. Indeed, for water transport in viscous aqueous sucrose, the estimates from Stokes-Einstein are more
than an order of magnitude off at viscosities higher than 100 Pa·s. This breakdown of the Stokes-Einstein description emphasizes the need to make direct measurements of diffusion: whilst the relation may be applicable at low viscosities or for large molecules,

![Figure 5-3 Diffusion coefficients of water in SOM.](image)

Experimental datapoints are shown as colored circles, with the difference in color between the background and circle interior showing the difference between the fit and the measured data. Adopted from Price et al. [2015].

it fails to predict water diffusion coefficients in highly concentrated SOM. Finally, we compare our water diffusion coefficient measurements with estimates produced using a model based on percolation theory [Shiraiwa, Zuend, et al., 2013], using an assumed water diffusion coefficient in SOM at $a_w = 0$ the same as that of sucrose at $a_w = 0$. The experiments performed at University of Leeds also show that water diffusion in $\alpha$-pinene SOM to be faster than in sucrose solutions at the same water activity and temperature, possibly explaining the discrepancies between the measured data and percolation theory estimate.
The collaboration between Harvard and University of Leeds shows that the data measured in Chapter 4 is useful for estimating the diffusivity of large gas phase molecules, while for smaller molecules, such as water, the Einstein Stokes Equation may not stand anymore. Further results on other gas phase molecules, such as ozone, is needed. It is also important to note that the time scale for diffusion strongly depends on size, therefore a 100 nm aerosol particle of the same material under the same conditions will take much less time than a particle with 1 um diameter to equilibrate.

5.3.3 Influence of Relative Humidity on the Molecular Structure of Secondary Organic Material

For this section, the sample collection was performed at Harvard and the SFG analysis was conducted at the Northwestern University [Shrestha et al., 2014]. A brief description of the experimental procedure is shown here: the SOM-deposited and SOM-pressed windows were used in a home-built RH-controlled flow system (Figure 5-4). Helium gas was sent across the SOM-containing optical windows via a dry and a humidified flow line, with the latter consisting of a bubbler containing Millipore water.
Mass flow controllers (MKS) connected to an A/D converter (MKS, Type 247) were used to regulate the Helium flow through the two lines under the constraint of constant He flow such that a desired RH value, measured by a calibrated RH meter (Omega Engineering, RH-USB, 2% to 98% RH range, uncertainty of ± 3 percentage points), was reached. Measured RH values of 95 %, termed "wet", and below 2%, termed "dry", were employed in this study, and RH jumps between these values took about two minutes using our sample cell, which has an internal volume of approximately 10 cm$^3$.

**Figure 5-4 Experimental setup of the SFG cell geometry.** Adopted from Shrestha et al. [2014]
For the samples studied here, standard resolution (10-15 cm\(^{-1}\)) SFG spectroscopy and directed both a broadband infrared and a visible beam through the CaF\(_2\) window at incident angles of 60° and 45°, respectively, while also overlapping them in time and space to generate SFG signals that oscillated at the sum of the two input frequencies (Figure 5-4). After accounting for refraction of the beams through the CaF\(_2\) window, the incident angles of the infrared and visible beams at the SOM/CaF\(_2\) interface were 38.8° and 30.4°, respectively. The infrared light field was tuned to the C–H stretching region to probe the SFG signal arising from the C–H oscillators located at the SOM/air interface, with negligible signal contributions from internal interfaces [Carlena J. Ebben et al., 2013]. Given that the Fresnel coefficients that determine how many SFG signal photons are transmitted from the interface to the detector depend on the difference in refractive index, the SFG signal detected here was mostly due to the interfacial regions characterized by the largest refractive index changes, which in this case was the interface between the gas phase and the particle material on the window.

The SFG spectra were collected using the ssp (s=light field plane-polarized perpendicular to the plane of incidence, p=light field plane-polarized parallel to the plane of incidence, listed in the order of the SFG, the upconverter, and the infrared frequencies) polarization combinations to probe those vibrational mode components that are orientated parallel to the plane of incidence. ppp-Polarized SFG spectra are recorded as well to probe for molecular orientation changes. A complete description of the standard (10-15 cm\(^{-1}\)) and sub 1-cm\(^{-1}\) resolution SFG spectrometers used here is provided elsewhere [C. J. Ebben, Martinez, Shrestha, Buchbinder, Corrigan, Guenther, Karl, Petaejae, et al., 2011; C. J. Ebben, M. Shrestha, I. S. Martinez, A. L. Corrigan, A. A. Frossard, W. W. Song, D.
R. Worton, T. Petaja, et al., 2012; M. Shrestha et al., 2013; Velarde et al., 2011. The sub-1-cm\(^{-1}\) resolution SFG spectra were collected with the incident angles of infrared and visible incident angles on the CaF\(_2\) window at 55\(^\circ\) and 45\(^\circ\), respectively, as shown in Figure 5-5.

The intensity of the SFG signal, \(I_{\text{SFG}}\), is proportional to the square modulus of the second order nonlinear susceptibility, \(\chi^{(2)}\), and the energies of the incident upconverter pulse, \(E_{\omega}\), and the infrared, \(E_{\nu}\) [Eisenthal, 1996; Geiger, 2009; Richmond, 2001; Shen, 1984]. The second order nonlinear susceptibility depends on the number of SFG-active C–H oscillators on the SOM surface, \(N_{\text{surf}}\), and the average molecular orientation distribution of their molecular hyperpolarizability, \(\beta\), according to

\[
\sqrt{I_{\text{SFG}}} \propto E_{\text{SFG}} = \chi^{(2)} E_{\omega} E_{\nu} = N_{\text{surf}} \langle \beta_{\text{C-H}} \rangle
\]  

(5-4)

Given that the visible pulse energy was less than 1 \(\mu\)J and held constant, and given that the number of SOM-containing particles in the laser spot was constant under most conditions (\textit{vide infra} for exceptions), any changes in the SFG spectra were attributable to changes in the average molecular orientation distribution of the C–H oscillators at the SOM surface. ssp-Polarized SFG spectra were collected for a given SOM sample at a particular RH value for at least 10 minutes, with each spectral acquisition time lasting two minutes. The acquisition time for each ppp-polarized spectrum was 4 minutes long. Following our previously described data workup procedures [C. J. Ebben, Martinez, Shrestha, Buchbinder, Corrigan, Guenther, Karl, Petaejæ, et al., 2011; C. J. Ebben, M. Shrestha, I. S. Martinez, A. L. Corrigan, A. A. Frossard, W. W. Song, D. R. Worton, T. Petaja, et al., 2012; M. Shrestha et al., 2013], we reported here the average of five SFG spectra for each RH condition ("wet" or "dry").
Figure 5-5 shows the SFG spectra obtained by Northwestern from a SOM sample on a CaF$_2$ window, which was collected on a Teflon filter using the flow tube, then pressed against the window and subsequently removed from the filter. The spectrum shown in was collected by centering the spectral range of the IR light around 2940 cm$^{-1}$ with a bandwidth of approximately 120 cm$^{-1}$ to cover the strong and weak modes at 2940 cm$^{-1}$ and 2870 cm$^{-1}$. The advantage of this approach is that the spectrum can be recorded in 2 minutes, so as to track the SFG response during RH jumps in close to real time.

![Figure 5-5 ssp-Polarized SFG spectra of sample 1 collected in ‘narrow-band’ mode during exposure to <2% RH (grey) and 95% RH (blue). Adopted from Shrestha et al. [2014]](image)

Figure 5-5 shows ssp-polarized SFG signal intensity decreases in the narrow-band spectral range probed upon increasing the RH increases from <2% to 95% RH. At 95% RH, the SFG signals from O–H oscillators of water molecules adsorbed to the SOM surface could interfere deconstructively with the C–H oscillators of the SOM surface.
species, thus leading to the observed SFG signal intensity reductions observed under "wet" conditions. Such spectral interference has been reported for a variety of air/water interfaces containing surfactant monolayers [X. Chen, Hua, Huang, & Allen, 2010; Mondal, Nihongyanagi, Yamaguchi, & Tahara, 2012]. Thus deuterium oxide was used to replace the water in the bubbler. Given that D$_2$O has a slightly lower saturation vapor pressure (2.0 kPa) than water (2.3 kPa) at 20°C [Hill & MacMillan., 1980; Matsunga & Nagashima, 1987], the D$_2$O experiments were carried out at 91±1% RH. The SFG responses observed for H$_2$O persist when using D$_2$O; two different particle samples showed an average percent increase of 18 ± 6% at low RH compared to the high RH. These results provide conclusive evidence that changes in the SFG signal intensities are not due to spectral interference between O-H and C-H oscillators at the SOM surfaces.

The experiments also considered the effects of the refractive index on Fresnel coefficients. The refractive indices based on the Ciddor equation of room-temperature air in the visible wavelength are 1.000271800 and 1.000267394 at 0% RH and 100% RH, respectively [Stone & Zimmerman, 2001]. Liu et al. reported a refractive index for pinene-derived SOM of 1.49-1.52 at 550 nm [Liu et al., 2013]. By employing Snell’s law of refraction [Alonso & Finn, 1988] and by calculating the Fresnel coefficients at 100% and 0% RH using the known refractive index values, we estimated the ratio of the ssp-polarized SFG intensities at high RH and low RH to be close to 1.00, indicating that refractive index changes in air for the two different RH conditions are not large enough to rationalize the differences in the SFG signal intensities observed in Figure 5-5. Therefore those changes in the SFG signal intensity that occur when SOM is subjected to "dry" vs. "wet" conditions are due to changes in the molecular orientation distributions of the
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various SFG-active C–H oscillators. Of a total of 23 "wet" to "dry" experiments and 14 "dry" to "wet" experiments, 29 lead to an increase of at least 10% in the SFG response at <2% RH when compared to the "wet" condition, irrespective of the jump direction. This type of response is termed as the "majority response", while SFG signal increases less than 10% when comparing 95% RH to <2% RH are termed as the "minority response". Figure 5-6 shows the time-dependent experiments and the change in the SFG "majority response" is instantaneous given the spectral acquisition time we employed in the experiment (2 minutes). Meanwhile, the ppp-polarized SFG spectra show no signal intensity change upon changing RH, irrespective of whether ssp-polarized response fall into the "majority response" or "minority response" category. Equation 5-4 indicates that there may be two causes for any observed change in the SFG signal intensity of a system of C–H oscillators. First, the number of C–H oscillators probed by our system. Given the

![Figure 5-6 Time-dependent experiment conducted that shows the increase in signal intensity as the RH is transitioned from 95% to <2% .](image)

Adopted from Shrestha et al. [2014].
number of particles remained constant in the experiments and assuming that organic material did not get lost from a given particle during the humidification-drying cycles, we can conclude the total number of C–H oscillators per particle remained constant. To estimate how many of the oscillators present at the surface of a dry particle remained at the interface upon humidification we had to account for the hygroscopic growth of the particle. As shown in Figure 5-6, the total number of C–H oscillators per particle did not change during the hygroscopic growth but the particle volume and the exposed surface area both increased. The published hygroscopic growth factors for α-pinene-derived SOA particles range from 1.05 to 1.12 at 95% RH [Varutbangkul et al., 2006; Wex et al., 2009], leading to a potential reduction in the density of the C–H oscillators by a factor ranging from 1.16 to 1.40 under "wet" conditions when compared to "dry" conditions. However, it is probably incorrect to assume that the number of the C–H oscillators in the SFG-probed surface layer should drop by the same factor because the surface-active α-pinene oxidation products may cover the surface nearly as densely as they do in a dry particle. Along the same line of thought, increased water content in the particles is unlikely to drive surfactant-like compounds from the particle bulk to the surface when compared to dry conditions, as that scenario would result in SFG signal increases at high vs. low RH. Conversely, if the increased water content in the SOM under "wet" conditions were to result in the displacement of organic species from the SOM surface, where they are SFG active, to the SOM bulk, where they would be SFG inactive, the resulting SFG signal intensity decreases would occur across all polarization combinations surveyed. This scenario is unlikely as the ppp-polarized SFG spectra does not change as the RH is cycled between 95 and <2%.
The second factor in Equation 5-4 explains the molecular orientation distributions of the SFG active C–H oscillators. Given that SFG signal intensity reductions are generally associated with increased surface disorder and concomitant loss in net polar alignment of oscillators under conditions of mass conservation, the SFG signal decreases observed under "dry" vs. "wet" conditions was attributed to substantial changes in SOM surface disorder [A. M. Buchbinder, E. Weitz, & F. M. Geiger, 2010]. This interpretation of our observations is supported by reports of marble- vs honey-like properties of SOM, in terms of its viscosity, under low vs. high RH conditions [Hallquist, Wenger, Baltensperger, Rudich, Simpson, Claeys, Dommen, Donahue, George, Goldstein, Hamilton, Herrmann, Hoffmann, Inumaa, Jang, Jenkin, Jimenez, Kiendler-Scharr, Maenhaut, McFiggans, Mentel, Monod, Prevot, et al., 2009; Kidd et al., 2014e; Renbaum-Wolff et al., 2013a; Seinfeld & Pandis, 2006a]. Using this interpretation, well-ordered SFG-active C–H oscillators are described by a narrow molecular orientation distribution of the molecular hyperpolarizability tensor, $\beta$, under "dry" conditions,
whereas "wet" conditions broaden the orientation distribution, and thus lower the second order susceptibility, as shown in Figure 5-7.

5.4 Conclusions

In this work, laboratory-generated SOM is collected at the Harvard flow tube and then were sent to collaborators at University of Leeds and Northwestern University for spectroscopic analysis. SOMs collected under high concentrations of precursors has some known differences to atmospheric SOM: it is typically less oxidized and more volatile than ambient particles [Neil M. Donahue et al., 2012]. Higher oxygen to carbon ratio in α-pinene SOM correlates with higher \( T_g \) [Berkemeier et al., 2014], indicating that atmospheric SOM may be more viscous than the SOM studied here. Recently, O'Brien et al. (2014) found that viscosity and/or surface tension could be higher in ambient organic particles than laboratory-generated SOM, attributing this to variations in chemical aging time and the complexity of field aerosol. Assuming that higher viscosity is associated with slower diffusion, this implies that the diffusion coefficients of water in atmospheric SOM might be lower than those we measured in our laboratory study. On the other hand, the duration of our experiments may lead to the unavoidable evaporation of some semi-volatile components of SOM, which may have the effect of decreasing the measured diffusion coefficients. We used only the water-soluble component of SOM that was generated at low RH, from a single precursor, and this cannot necessarily be assumed to be characteristic of real atmospheric SOM. However, water-soluble material represents the major fraction of α-pinene SOM [Renbaum-Wolff et al., 2013a], and these results are currently the only direct measures of water diffusion in this material. The presence of less water-soluble species would reduce the hygroscopicity of SOM, possibly increasing the
viscosity and decreasing diffusion coefficients by lessening the plasticising effect of water. It should be emphasized that we have measured the diffusion of water, a highly mobile component, but the diffusion of larger organic molecules in SOM is much slower [Abramson et al., 2013; Zhou et al., 2013], and may lead to inhibition of condensed-phase chemistry in situations where water diffusion is unimpeded and a kinetic limitation on gas-particle partitioning of SVOCs. Future work should focus on measuring the diffusion of larger molecules in SOM.

This study highlights the importance of directly measuring diffusion in order to determine how water is transported in SOM. We have shown that water diffusion is not kinetically limited in the water-soluble component of α-pinene SOM at 280K, but slows dramatically as temperatures decrease. Under conditions relevant to the upper troposphere, radial variations in phase develop which may have important consequences for aerosol chemistry and ice nucleation. The role of slow diffusion in SOM needs to be explored further in order to quantify its impact on atmospheric chemistry and climate.

For SFG surface analysis, we have shown that SFG spectrum from SOA particles prepared from the ozonolysis of α-pinene and collected by electrostatic impactors at the Harvard flow reactor. Preliminary results indicate the C–H oscillators of α-pinene-derived SOM deposited on CaF$_2$ windows switch back and forth between two different molecular orientation distributions in a reversible fashion as the RH is lowered or raised. The orientation distribution at high RH, along with the possible decrease in C–H oscillator density (but not number) per SOM-containing particle, is likely to represent a less dense arrangement of organic compounds at the particle surface, through which transfer of molecular species exchanging between the aerosol particle phase and its gas
phase is more facile at 95% RH when compared to <2% RH. The absence of a reliable and definite assignment of the SFG spectral features currently precludes an analysis regarding molecular orientation angles and their distributions from the ratio of the SFG amplitudes obtained from the ssp- and ppp-polarized spectra.

The two studies above show that effects of water vapor to SOM particles generated from $\alpha$-pinene ozonolysis in the flow tube reactor. Water not only changes the diffusive rate of gas phase species (including itself) into the particles, but also alters the molecule orientations at the surface of the particles, which further affects the absorption and adsorption of gas phase species to the particle phase. Considering the diurnal cycling of the RH in the atmosphere, the effects of water to SOM particles may play an important role in aerosol chemistry, number-diameter distribution, and reactivity. Further studies involving researching the RH impacts on the aerosol modeling process are needed.
6. Conclusion and Outlook

SOMs generated from BVOCs accounts for a great portion of global particulate matter, especially over the tropical rainforest, where the percentage can be as high as 90% [Q. Chen et al., 2009]. As one of the major components of BVOCs, monoterpenes play an important role in forming SOMs due to its high reactivity as well as relatively high concentration [C. J. Ebben, Martinez, Shrestha, Buchbinder, Corrigan, Guenther, Karl, Petaja, et al., 2011; Heaton et al., 2009; Yáñez-Serrano et al., 2015]. The work of this thesis has analyzed the physicochemical properties of SOM particles generated from ozonolysis of α-pinene, one of the major components of monoterpene, by using a flow tube reactor, particle measurement instruments, and spectroscopic techniques. The results answer questions such as whether precursor chirality can affect aerosol physical properties, as well as the influence of viscosity on aerosol growth and their chemical reactivity, both of which contribute greatly to the scientific community on the physicochemical properties of SOM.

Chapter 2 gave a detailed description of the flow tube reactor, which is one of the primary instruments used in this thesis. A matrix of precursor concentrations spanning 3-4 orders of magnitude was experimented on in this study to determine the optimal concentrations for particles to undergo condensational growth and coagulational growth. The time evolution study also characterized the size and concentrations of the particles at different positions of the flow tube reactor, providing further evidence to distinguish condensational growth from coagulational growth. Particles with sizes of 93 ± 3 nm, prepared using 51 ± 1 ppm O₃ and 1.0 ± 0.03 ppm pinene, were formed in the flow tube under mainly coagulative growth conditions at particle number concentrations of (1.1 ±
0.1) \times 10^6 \text{ particles cm}^{-3} \text{ with a total mass of } (1.2 \pm 0.1) \times 10^3 \text{ ug m}^{-3}. \text{ Particles with sizes of } 63 \pm 3 \text{ nm, prepared using } 51 \pm 1 \text{ ppm O}_3 \text{ and } 0.125 \pm 0.001 \text{ ppm } \alpha\text{-pinene, were present in the flow tube at particle densities of } (9.5 \pm 0.7) \times 10^4 \text{ particles cm}^{-3} \text{ with a mass concentration of } 12 \pm 2 \text{ ug m}^{-3}. \text{ This latter set of precursor concentrations produced mostly condensationally grown particles, whereas coagulative conditions became important for particles prepared using the higher ozone concentrations.}

Chapter 3 introduces the hypothesis that the stereoisomers of \( \alpha\text{-pinene} \) can be retained in the secondary products during \( \alpha\text{-pinene ozonolysis} \). The enantiomeric mixed secondary products with opposite chirality can influence the spatial structure of the long chain oligomers and thus affect the physical properties of the SOM particles, including the number-diameter distributions. \text{ The experiments were conducted at an } \alpha\text{-pinene concentration of } 125 \pm 3 \text{ ppb and ozone concentration of } 21 \pm 3 \text{ ppm. The ratio between the } (+) \text{ and } (-)\text{-}\alpha\text{-pinene was varied between 98:2, 50:50 and 2:98. After stabilizing the temperature and minimizing the fluctuation of the total volume concentration, the number-diameter distributions of the SOM particles generated from the } (+) \text{ and } (-) \text{ 50:50 mixed precursor did not show a statistically significant difference compared to the two quasi-pure enantiomers. The result demonstrates that the effects of enantiomeric precursors on the number-diameter distribution of SOM particles are within the detection limit of our instrument, suggesting a limited influence of chirality on the aerosol growth process. Further experiments on the other properties of the SOM generated from chiral precursors, such as CCN activity and hygroscopicity, are needed.}

Chapter 4 develops a new method that can determine the viscosity of submicron, atmospherically-relevant organic particles while they are still suspended as an aerosol. A
particular advantage of this method is that there are no further post-processing techniques that have been suspected of altering the properties of the semivolatile particles.

Laboratory experiments were coupled with numerical simulations to obtain the viscosities of the suspended submicron particles as a function of RH. The particles are produced by the ozonolysis of α-pinene. The viscosity drops from $10^{(8.7 \pm 2.0)}$ to $10^{(7.0 \pm 2.0)}$ Pa s (2σ) as RH increases from <5% to 58% at 293 K. These results imply that the equilibration of the chemical composition within submicron, climatically relevant atmospheric particles with the chemical composition of the gaseous phase can shift from hours at mid-range RH to weeks for low RH. However, the upper limit of the viscosity that can be measured in this study is determined by the merging time of the aerosol particles that can be observed through the environment. Future studies must employ a shorter residence time flask in order to successfully measure particles with lower viscosities at high RH.

Chapter 5 used particle samples collected from the flow tube reactor through Teflon filter and the precipitator to study the effects of water on SOM diffusivity and surface properties. One study, in collaboration with the University of Leeds, measured the diffusivity of water in the water-soluble component of α-pinene derived SOM. The diffusion coefficient of water changes approximately from $10^{-12}$ to $10^{-14}$ m$^2$ s$^{-1}$ when the water activity changes from 0.8 to 0.2 at 280K. The measured diffusivity is 8 orders of magnitudes higher than the diffusivity predicted by the Einstein Stokes Equation. The result implies the Einstein Stokes Equation breaks down for smaller molecules, such as when calculating the diffusion coefficient of the SOM. Another study, in collaboration with Northwestern University, observed the change in surface properties of SOM particles at high and low RH by using spectroscopic techniques. The surface molecules
Conclusions and Outlook

are highly ordered when the SOM is exposed to low RH environment and are significantly less ordered when the RH increases. The surface properties of the SOM can affect the diffusion of gaseous phase species and thus change the SOM reactivity. Further analysis using isotope-labeled SOMs would enable us to measure molecular orientation angles and their surface molecule distributions.
Appendix A: Sensitivity Analysis of the COMSOL Model

To obtain uncertainty bars on the estimated viscosities, sensitivity analyses were performed for the numerical simulation of the change in particle shape. The analysis is organized in the following paragraphs as the effect of uncertainty in surface tension, the effect of the linear assumption for $\xi(\chi; X)$ of Eq. 4-9 and the effect of uncertainty in the initial particle shape.

The effect of surface tension $\sigma$ was tested for $2 \times 10^{-2}$ (low), $5.5 \times 10^{-2}$ (literature value), and $7.0 \times 10^{-2}$ (high) N m$^{-1}$. The central value represents the average of 83 organic compounds [Korosi & Kovats, 1981]. The low value is also within the envelope of the distribution of the 83 compounds. The high value is an upper limit approaching the surface tension of the water ($7.2 \times 10^{-2}$ N m$^{-1}$). The effect of $\sigma_{\text{low}}$ and $\sigma_{\text{high}}$ relative to $\sigma_{\text{central}}$ on the estimated viscosity is plotted in Figure A-1. The results show that the variation in surface tension altered the optimized viscosity by up to $\pm 0.2$ (log$_{10}$ units).

The effect of assuming a linear regression for $\xi(\chi; X)$ (i.e., Eq. 4-9) was evaluated by testing the analysis using other functional forms (Panel B, Figure A-1). Upper and lower tilted parabolic functions were used for comparison. The functional forms were constrained by $\{\varsigma = 0.75, \chi = 0.25\}$ for the upper parabola and by $\{\varsigma = 0.25, \chi = 0.75\}$ for the lower parabola, in addition to the endpoint pairs $\{\varsigma, \chi\}$ used in the linear regression. Difference in the assumed regression function led to a $\pm 0.1$ (log$_{10}$ units) uncertainty in the optimized viscosity.

The effect of assumptions about initial particle shape was evaluated by considering different scenarios of the initial extent of overlap (Panel C, Figure A-1). The
Appendix A: Sensitivity Analysis of the COMSOL Model

Figure A-1 Sensitivity analysis of the numerical simulation of material flow

scenarios, applied to both the dimer and trimer agglomerates, were based on the variability observed in the scanning electron micrographs. Scenario one employed the
same monomer diameter as the base case but decreased the overlap to 3 nm. Scenario two was the base case, representing an overlap of 5 nm. Scenario three considered larger monomers of 100 nm but of increased overlap of 30 nm. In this way, total volume was conserved compared to the base case. The scenarios were associated with an uncertainty of ±0.2 (log₁₀ units) in the optimized viscosity.

The combined maximum uncertainty of the foregoing factors is shown as the overall error bars on the viscosity values plotted in Figure 4-14. A detailed version of Figure 4-14, in which the uncertainty of each factor is color-coded along the error bar is shown in Figure A-2.

![Figure A-2 Viscosity of α-pinene derived SOM from 5-58% RH.](image)

The error bar represents the relative contribution of different factors to the uncertainty estimates. The color coding in the legend shows the relative contributions of geometric factors, surface tension, particle shape (i.e., dimer or trimer), and regression model. Each uncertainty is represented as a line segment, and the total uncertainty is the sum of the length of the line segments. For the base case, Part I is developed for dimer algomerates and Part II for trimer algomerates.
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