**Supplementary Information**

**Changing Shapes and Implied Viscosities of Submicron Suspended Particles**

Yue Zhang1, Mariana S. Sanchez1,2, Claire Douet1,3, Yan Wang1,4, Adam P. Bateman1, Zhaoheng Gong1, Mikinori Kuwata1,5, Lindsay Renbaum-Wolff6, Bruno B. Sato1,7, Pengfei Liu1, Allan K. Bertram6, Franz M. Geiger8,\*, and Scot T. Martin1,9,\*

1School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, USA 02138; 2Department of Chemical Engineering, University of São Paulo, São Paulo, Brazil 05508; 3Department of Energy and Environment, National Institute of Applied Science of Lyon, Villeurbanne, France 69100; 4School of Public Health, Harvard University, Boston, Massachusetts, USA 02115; 5Earth Observatory of Singapore, School of Physical and Mathematical Sciences, College of Sciences, Nanyang Technological University, Singapore 639798; 6Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Z1; 7Department of Chemical Engineering, Federal University of Sao Carlos, Sao Carlos, São Paulo, Brazil, 13565; 8Department of Chemistry, Northwestern University, Evanston, IL, USA 60208; 9Department of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts, USA 02138.

January 2015

Atmospheric Chemistry and Physics

*Corresponding authors:* Scot T. Martin, (617) 495-7620,scot\_martin@harvard.edu,

Franz M. Geiger, (847) 467-6553, geigerf@chem.northwestern.edu

**S1. Dynamic shape factor**

The dynamic shape factor χ was calculated as follows (DeCarlo et al., 2004):

(S1)



for an envelope shape factor *κ*, a porosity factor *δ*, a Cunningham correction factor *C*c, and a mass-equivalent diameter *d*me. The diameter was calculated from particle mass *m*p, as follows (Kuwata and Kondo, 2009; Zelenyuk et al., 2006):

(S2)



for a particle material density *ρ*. The term *C*c(*z*) was calculated as follows (Dahneke, 1973):

(S3)



where λ is the mean free path of air at 293 K (6.64 × 10-8 m) and *z* is the argument (i.e., either *d*me or *δd*me). The relationship of *m*p to the APM voltage *ϕ* and angular velocity ** was obtained as follows:

(S4)



for the number *q* of charges on the particle, the value *e* of an elementary charge, and inner and outer radii *R*1 and *R*2, respectively, of the cylindrical channel of the APM (Ehara et al., 1996; Kuwata and Kondo, 2009). The envelope shape factor *κ* of Eq. (S1) was calculated as follows (DeCarlo et al., 2004):

(S5)



for a mobility diameter *d*m, as selected by the DMA.

Combination of Eqs. (S3) and (S5) leads to the following overall expression for the dynamic shape factor (DeCarlo et al., 2004):

(S6)



The porosity factor cancels out. Terms *d*m and *m*p are the experimental parameters of the DMA-APM apparatus. The material density *ρ* is taken as 1050, 1770, and 1200 kg m-3 for PSL, ammonium sulfate, and α-pinene SOM, respectively (Kuwata et al., 2011). A sensitivity analysis is presented in Section S3concerning the influence of *ρ*SOM on the calculated shape factor.

**S2. Calibration**

*APM mass calibration.* Polystyrene latex (PSL) particles purchased from commercial sources are of known diameter and material density and, hence, mass. An example of the apparent number-mass distribution of PSL particles is shown in Figure S4. The apparent mass was obtained for the instrument settings using Eq. (S4). The peak of the distribution was calculated by fitting to a Gaussian function. Measurements were performed three times for each selected mobility diameters of PSL particles (52.4, 74.0, 85.6, 93.5, and 126.0 nm). The apparent mass differed by 3% from the expected mass (cf. vertical lines in Figure S4). The APM data collected during the experiments were adjusted by this percentage.

*DMA-APM shape factor calibration*. With the APM mass adjustment in place, the calibration of the DMA-APM with respect to measurement of the dynamic shape factor χ was checked by selecting PSL particles with the DMA and using Eq. (1). Figure S5 shows the χ values for different mobility diameters of PSL as well as different relative humidities for both PSL and ammonium sulfate particles. The expected χ based on literature is 1.00 for PSL particles (Allen and Raabe, 1985) and on order 1.02 for ammonium sulfate particles (Table S1) (Li et al., 2003; Biskos et al., 2006), in agreement with the results show in the figure. The dynamic shape factor of PSL particles was measured as 1.00 ± 0.01 (two sigma) for all five diameters ranging 46 to 125 nm. Taken together, these results suggest an uncertainty of the DMA-APM instrument train of ±0.01 (two sigma) for determination χ. The results also demonstrate an absence of any shift in the calibration with RH.

**S3. Sensitivity analysis for material density**

Given that the material density of the SOM was not directly measured in this study and that the value (1200 kg m-3) was instead taken from literature under related but not identical reaction conditions (Shilling et al., 2009), a sensitivity analysis was conducted to test the effect of material density on the shape factor obtained by Eq. (1). Figure S6 shows the results. Literature results suggested a central value of 1200 kg m-3 for the high mass concentrations of the present study, and importantly Figure S6 shows that for this material density χ trends to 1.00 at high RH, as expected. Figure S6 also shows that the shape factor varies on order of 0.03 for an uncertainty of 50 kg m-3 in material density. The uncertainty in material density represents a possible systematic error, with the associated implication for the present study that relative differences in χ for the different experimental conditions remain unchanged.

**S4. Factors influencing the dynamic shape factor of synthesized particle populations**

*Precursor concentration and mobility diameter.* The data presented in the main text relate mainly to the optimized conditions of synthesis that led to a particle population of a high dynamic shape factor. This condition was found by empirically exploring the range of factors that influence the shape factor. The present section presents the range of synthesis conditions that was explored and the associated shape factors that were obtained.

The dependence of shape factor on mobility diameter is shown in Figure S7for three different initial concentrations of α-pinene (<5% RH). Although all particle populations had shape factors greater than 1.00, the extent of asphericity was different. Relatively low (500 ppb) and high (1000 ppb) precursor concentrations were associated with relatively small dynamic shape factors for all diameters. By comparison, an intermediate (700 ppb) precursor concentration led to relatively large dynamic shape factors for some diameters. The optimized conditions of the main text are presented for this maximum at 126.0 nm.

The influences of precursor concentration and mobility diameter on shape factor are tightly coupled to the effects on particle coagulation. For 500 ppb α-pinene, there were lower number concentrations and hence there was decreased coagulation within the particle population, favoring more spherical particles. For 700 ppb, there was increased coagulation, and thus dimer and trimer agglomerates were more common. Multiple SEM images showing this result are presented in Figure 8. For 1000 ppb α-pinene, the particle number concentration was higher, increased coagulation occurred, and polyhedral particles were produced. Given the number concentrations and mode diameters, collision frequencies for 500, 700, and 1000 ppb are estimated as 2.5 × 10-4 s-1, 5.5 × 10-4 s-1, and 6.0 × 10-4 s-1 (Seinfeld and Pandis, 2006), respectively, although these are lower-limit estimates because they are based on particle concentrations and mode diameters downstream of the flow tube and coagulation plenum.

*Relative humidity*. The effect of relative humidity on the shape factors of all of the different SOM particle populations is shown in Figure S9. For the cases having an aspherical shape factor at low RH (i.e., beyond measurement uncertainty), a general feature is a decrease in shape factor for increasing RH.

*Particle Composition.* 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 CO2 were compensated by the approach of Collier and Zhang (2013). Elemental ratios were determined using the method of Canagaratna et al. (2014), and the results agree well with the previous measurement of similar mass loading (Chen et al., 2011). The diameter independence of the results for the O:C and H:C elemental ratios, plotted in the Figure S10, 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 by Eq. (1) would have become more complicated. The results plotted in Figure S10 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.

**S5. Viscosity estimated by flow simulation**

The procedure for estimating viscosity from the data sets was as follows.

1. The dimer and trimer geometries ofFigure S3 were evaluated as base cases I and II for the model. The sensitivity analysis of Section S6 considers other geometries. For both base cases, the geometry was described by the longest axis *L*1 and the shortest axis *L*2 (cf. Figure S3).

2. A geometry factor *ξ*, defined as *ξ* = (*L*1/*L*2)2, was used to quantify particle asphericity. The rationale for defining *ξ* is that and 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, *ξ* describes a sphere. The geometry progressively deviates from spherical for larger *ξ*. The upper limit of *ξ* is four or nine for the tangential limits of dimer and trimer geometries, respectively.



3. For the base cases, *ξi,*I was 3.78 for the dimer and *ξi,*II was 8.12 for the trimer. The subscript *i* denotes the initial geometry at time zero.

4. 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 *ξf* was calculated. The subscript *f* denotes the final geometry. This process was repeated for a full range of viscosity values.

5. The results are plotted in Figure S11A for the viscosity on the ordinate and the geometry factor on the abscissa so that a function *η*(*ξf*;*X*) is described. The parameter *X* specifies case I or II. The curves of *η*(*ξf*;*X*) for the two base cases were empirically fit, as follows:

(S7)



for fitting coefficients *a* through *e*. Equation (S7) shows that a final geometry shape factor implies an associated estimated viscosity.

6. For each of I and II, there is a monotonic relationship between the geometry factor *ξ*(*X*)and the aerodynamic dynamic shape factor *χX*. In implementation, only the endpoints were constraint, and a linear relationship between them was assumed, as follows:

(S8)



for fitting coefficients *m* and *q*. Equation (S8), which holds for all times (e.g., both initial and final), shows that an aerodynamic dynamic shape factor implies a geometry shape factor. For case I, fitting coefficients to calibrate Eq. (S8) were found by the constraints of {*ξi* = 3.72, *χ* = 1.19} at time zero and {*ξf* = 1, *χ* = 1} at long time. For case II, the constraints were given by {*ξi* = 8.12, *χ* = 1.26} at time zero and {*ξf* = 1, *χ* = 1} at long time. The constraints at time zero were based on the data sets of Figure 4B (i.e., <5% RH corresponding to zero exposure time to elevated RH). The fits are plotted in Figure S11B. The assumption of a linear relationship is examined in the sensitivity analysis of Section S6.

7. Combination of Eqs. (S7) and (S8) leads to the following result:

(S9)



The shape factors *χf*,*X* were the final values after exposure to an elevated RH. The cases I and II plotted in Figure 6 represent the application of Eq. (S9) to each of the data points of Figure 4B.

**S6. Sensitivity analysis for estimated viscosity**

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 of Eq. (S8), and the effect of uncertainty in the initial particle shape (Figure S13).



The effect of surface tension σ was tested for 2 × 10-2 (low), 5.5 × 10-2 (literature valus), and 7.0 × 10-2 (high)N m‑1 (Panel A, Figure S13). The central value represents the average of 83 organic compounds (Korosi and 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 × 10-2 N m‑1). The effect of σlow and σhigh relative to σcentral on the estimated viscosity is plotted in Figure S12A. The results show that the variation in surface tension altered the optimized viscosity by up to ±0.2 (log10 units).

The effect of assuming a linear regression for (i.e., Eq. (S8)) was evaluated by testing the analysis using other functional forms (Panel B, Figure S13). Upper and lower tilted parabolic functions were used for comparison. The functional forms were constrained by {*ξ* = 0.75, *χ* = 0.25} for the upper parabola and by {*ξ* = 0.25, *χ* = 0.75} for the lower parabola, in addition to the endpoint pairs {*ξ*, *χ*} used in the linear regression. Difference in the assumed regression function led to a ±0.1 (log10 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 S13). The 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 6. A version of Figure 6 in which the uncertainty of each factor is color-coded along the error bar is shown in Figure S13.

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**Table** **S1.** Summary of calibration conditions and results

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Particles | Central Mobility Diameter  (10-9 m) | Central Particle Mass  (10-18 kg) | Dynamic Shape Factor | Calibration Error |
| PSL | 52.4 | 0.081 | 1.00 ± 0.01 | 1% |
| 74.0 | 0.226 | 1.00 ± 0.01 | 1% |
| 85.6 | 0.347 | 1.00 ± 0.01 | 1% |
| 93.5 | 0.459 | 1.00 ± 0.01 | 1% |
| 126.0 | 1.15 | 1.00 ± 0.01 | 1% |
| Ammonium Sulfate | 52.4 | 0.127 | 1.03 ± 0.01 | N/A |
| 74.0 | 0.362 | 1.02 ± 0.01 | N/A |
| 85.6 | 0.570 | 1.02 ± 0.01 | N/A |
| 93.5 | 0.753 | 1.01 ± 0.01 | N/A |
| 126.0 | 1.88 | 1.01 ± 0.01 | N/A |

**List of Supplementary Figures**

**Figure** **S1.** Number-diameter distribution of a particle population produced from 700 ppb α-pinene and 14 ppm ozone. The inset plot shows an expanded view of the number-diameter distribution from 110 and 140 nm. The red marker at 126.0 nm highlights that the mobility diameter selected by the DMA and subsequently sent to the APM draws from the larger side of the number-diameter distribution (i.e., dimer, trimer, and higher-order agglomerates).

**Figure** **S2.** 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 relative humidity. It consists of humidifying and drying components. SOM particles were brought to a controlled RH by using a Nafion 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 Nafion 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.

**Figure** **S3.** The base-case initial dimensions of dimer and trimer agglomerates used for modeling by computational fluid dynamics. The lengths of the longest and shortest axes of the agglomerates are defined as *L*1 and *L*2, respectively.

**Figure** **S4.** Number-mass distributions measured for a population of monodisperse polystyrene latex (PSL) particles (93.5 nm mobility diameter). The experiments were performed three times. The abscissa of apparent particle mass is calculated based on the APM rotation speed and the voltage applied between the walls of the APM cylinders (Eq. (S4)). The error bars represent two sigma. The lines represent fits of a normal distribution to the data. See further discussion of the vertical lines in the main text.

**Figure** **S5.** Dynamic shape factors measured for spherical particles (PSL) and slightly aspherical particles (ammonium sulfate). Panel A shows results for PSL particles of several different mobility diameters for <5% RH. Panel B shows results for particles of fixed diameter (126.0 nm) but increasing relative humidity. The particles were first exposed to various RH (as shown along the abscissa) and then dried to < 5% RH prior to measurement. The dashed lines in both panels represent a reference point for a shape factor of 1.00, corresponding to a spherical particle.

**Figure** **S6.** Sensitivity analysis of the effect of the uncertainty in material density on calculated shape factors (Eq. 1). 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 α-pinene and 14 ppm ozone). The dashed line represents a reference point for a shape factor of 1.00, corresponding to a spherical particle.

**Figure** **S7.** Examples of dynamic shape factors obtained for particle populations produced at different precursor concentrations (14 ppm ozone). The error bars represent two sigma.

**Figure S****8.** Scanning electron micrographs of particles of the two different mobility diameters corresponding to Figure 4B. Panel A shows images of particles collected from a particle population having a central mobility diameter of 126.0 nm. Dimer aglomerates dominate the particle population. Panel B shows images of particles collected from a particle population having a central mobility diameter of 165.0 nm Trimer or higher order algomerates (cf. images *b* - *h* and *k* - *n*) are the dominant particle type.

**Figure** **S9.** Full data set of dynamic shape factors measured in the present study for exposure to elevated relative humidity for 310 s. α-Pinene inflow concentrations of (A) 500 ppb, (B) 700 ppb, and (C) 1000 ppb. Corresponding ozone concentrations were 14 ± 1 ppm. The error bars represent two sigma.

**Figure** **S10.** 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.

**Figure** **S11.** Plots of Eqs. (S7) and (S8) showing the internal relations used in the numerical simulation (cf. Section S5).

**Figure** **S12.** Sensitivity analysis of the numerical simulation of material flow. Panel A shows the influence of assumed surface tension on optimized viscosity. Results for three different surface tensions (2 × 10-2, 4 × 10-2, and 7 × 10-2 N m-1) are plotted. Panel B shows the influence of the regression model (cf. Eq. (S8)) on the viscosity estimate. Panel C shows three scenarios of particle shapes. The first scenario consists of two 90-nm monomers having an overlap of 3 nm. The second scenario consists of two 90-nm monomers having an overlap of 5 nm. The third scenario consists of two 100-nm monomers having an overlap of 30 nm.

**Figure** **S13.** Relative contributions of different factors to the uncertainty estimates of the optimized viscosities. 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. The uncertainty estimates are based on the sensitivity analysis of Figure S13.

**Movie** **S1.** Full time series of flow simulation to accompany the initial and final snapshots of Figure 5.