

Response to reviews

Reviewer comments are in **bold**. Author responses are in plain text. Modifications to the manuscript are in *italics*. Page and line numbers in the responses correspond to those in the ACPD paper.

Reviewer #1

The manuscript “Changing shapes and implied viscosities of suspended submicron particles” by Y. Zhang et al., [2015] introduces a new approach for deriving in-situ the viscosity of suspended aerosol particles using α -pinene-derived secondary organic material (SOM) as model aerosol. The SOM viscosity is determined as a function of relative humidity (RH). Due to the inherently significant role viscosity plays in particle morphology, mixing state, and heterogeneous processes, and the potential applicability of the new approach to field particles, the article addresses a timely and important topic that would make a nice addition to the current scientific literature. The key difference compared to previous studies on this topic is the application of suspended aerosol particles instead of particles adsorbed onto substrates, which may avoid potential caveats. The paper (including supplement) is thorough and well-written. I have only a couple of comments regarding the approach that I hope the authors can address before publication in ACP.

We thank the reviewer for the careful reading of the manuscript and the associated questions and feedback that were provided. The revised manuscript takes into account these aspects. Detailed responses to each question are given below.

Specific comments

1. The authors should elaborate more why they chose to dry the particles following RH-conditioning in their flow setup and discuss potential caveats since the parameters used for deriving viscosity are based on DMA and APM measurements of the particle’s properties at a relative humidity of $\leq 5\%$. How would the dynamic shape factors and thus particle viscosity differ if the DMA and APM were maintained at the same RH as in the RH-conditioning region of the setup? I am mainly concerned that this extra drying step removes sufficient liquid water from the particles, suggesting that the derived viscosities for the high RH experiments may be overestimated compared to reality. There is only one sentence on the reasoning for not including the drying step, which is in regards to hygroscopic growth factors (Page 6830, lines 6-8), but very little discussion of the water partitioning behavior over the different RH regimes in the setup that I think would be crucial here. Please provide clarification or more discussion of this potential caveat.

The drying step highlighted by the reviewer has two purposes in the conducted experiments. The first is to avoid uncertainty in hygroscopic growth within the instrumentation, as discussed in the paper. The second is to “lock in” the shape of the particle after exiting the RH-conditioning region so that the shape changes ceases after a well-controlled residence time. For a contrary example, if the RH of the APM had been maintained at the same value as in the RH-conditioning region of the experimental setup, the dynamic shape factor would have continued to decrease (due to particle merging)

while particles traveled inside the tubing as well as in the APM, leading to uncertainties in sizing, in estimations of the extent of shape change, and hence in retrieved viscosities.

Section 3.2, first paragraph is revised as follows to clarify these points:

The particle populations of dimer, trimer, and higher-order agglomerates produced at low RH were subsequently exposed to elevated RH for a controlled residence time. At sufficiently high RH, the particle material flowed. The micrographs of column 2 in Fig. 1 show that nearly spherical particles resulted from exposure to sufficiently high RH. Correspondingly, spherical particles of unity shape factor resulted. The complete processing of the particle population was thus primary production, secondary coagulation for < 5 % RH, exposure of agglomerates to an elevated variable RH for a controlled time period, and instrumental characterization of shape factors for < 5 % RH. The final RH adjustment to < 5 % RH removed water from the particles, serving both to simplify interpretation of the sizing data of the DMA-APM and to freeze the particle shape after a controlled time period of possible material flow at elevated RH. This approach assumed that particle shape did not change with rapid removal of water, as was reasonable considering the overall scenario of the quick drying times relative to the slow material flow rates and the absolute water content of <1% by volume.

2. Viscosity as a function of RH is determined based on a fit of χ as a function of RH, such that when $\chi=1.00$ (defining a spherical particle), viscosity as a function of RH breaks down, which places a systematic limitation on the applicable RH range for a given particle system. Could the author's comment a bit more the inherent limitations of the approach? Since this paper introduces a new technique for determining the viscosity of suspended aerosol particles, the authors should at least comment on its applicability to other particle systems as a function of RH, ones that possess a different viscosity compared to α -pinene SOM.

We thank the reviewer mentioning that the discussions on the applicability and limitations of this method are needed. As the reviewer said, this method is based on shape change of the particles and therefore is limited by spherical shape. The method is not applicable to those viscosities from which the shape change would be shorter than the residence time of the RH-conditioning region, which indicates that there is a lower limit of the viscosity value that this method can measure. Particle size is also important. The time for merging to complete increases as the particle size increases. For particles that have similar size to this experiment (~100 nm), the viscosity values can be measured down to 10^4 Pa·s by using a small residence time (~10 s) and up to 10^{12} Pa·s by using a large residence time (~ 10 min). For particles with larger sizes, the viscosity can be measured down to 10^3 Pa·s.

A new paragraph is added to the revised manuscript to discuss these aspects:

The scope of applicability of the approach introduced herein to determine viscosity of submicron particles in aerosol form can be considered. The lower limit for the RH that can be probed is related to the first discernible detection of shape change within the exposure time to elevated RH. In the present study, for 45 s of exposure the lower limit of RH was 20 %. For 300 s, the lower limit was < 5 %. The upper limit is related to the full transformation to a spherical particle within the exposure time to elevated RH. In the present study, for 45 s of exposure the upper limit of RH was 58%. For 300 s, the upper

limit was 25%. The lower and upper limits for the viscosities that can be probed are related both to the particle diameter and the time for material flow (i.e., corresponding to the exposure time to elevated RH). For 100-nm particles, viscosities as low as 10^4 Pa s and as high as 10^{12} Pa s for exposure times on order of 10 s and 10 min, respectively, can be inferred by flow modeling to match shape changes. This viscosity range corresponds to varying degrees of semi-solidity. A future apparatus design for shorter residence times and larger particle diameters is an ongoing effort so that viscosity values can be probed at the transition point from semi-solidity to liquid.

Technical comments

1. Page 6823 lines 13-14: It is implied in the abstract that the particles transition from ‘solid’ to ‘semisolid’ over the RH range, which is a bit exaggerated. The particles become less-viscous over the applied RH range, but largely remain in a semi-solid phase state, e.g. [Koop et al., 2011].

The correction is added to the revised manuscript.

Based on particle diameter and RH exposure time, the viscosity dropped from $10^{(8.7\pm 2.0)}$ to $10^{(7.0\pm 2.0)}$ Pa s (2σ) for an increase in RH from < 5 to 58 % at 293 K.

2. Page 6824 lines 16-17: Regarding the discussion of particle phase and reactivity, references should be updated to include recent publications by Slade and Knopf [2014] and Arangio et al. [2015] regarding the impacts of viscosity, bulk diffusion, and OH multiphase kinetics.

We thank the reviewer for the comment. The excellent publication by Slade and Knopf is a very suitable citation and has been added to the main text. The publication by Arangio et al., although a good publication, does not strongly relate to our SOM-focused study.

3. Page 6827 lines 3 and 6: DMA and APM should be defined here.

The correction has been made

4. On page 6836, the last paragraph (lines 17-28) is a repeat of the end of the previous paragraph.

The end of the second-to-last paragraph is deleted.

5. Page 6848 (Fig. 4): It’s confusing that in the figure description for panel (b), particles are exposed to an RH up to 80%, yet in the actual figure the data points extend up to RH~100%. Furthermore, the viscosities reported in Fig. 6 only go up to RH=58%. Please clarify in the manuscript the reasons for these differences.

We thank the reviewer for the comment. The correction has been made as blow:

Correct of the Figure: *Panel (b): exposure up to 100 % RH for 45 or 310 s.*

Further explanation of the RH difference in section 3.3, first paragraph: *Please note that even though the RH was measured up to 100 % in the experiment (cf. Figure 4), the highest RH that could be studied (58 %) was limited by the full transformation to a spherical particle within the fastest experimental residence time (45 s).*

Review #2

Zhang et al. introduce a new experimental approach to estimate viscosities of suspended SOA particles. It is based on particle coagulation leading to dimer, trimer and higher-order agglomerates of non-spherical shape which eventually through plastic flow form spherical particles. The time needed to change shape is closely connected to viscosity allowing to retrieve RH dependent viscosity. In particular the technique can be used in situ which avoids some of the uncertainties of other techniques. This is a very nice piece of work, the paper is well written and the conclusions are supported by experiment. I recommend it for publication in ACP but ask the authors to take the following considerations into account.

We thank the reviewer for careful reading of the manuscript and for acknowledging the worth of the manuscript. The questions and comments are taken into account in the revised manuscript. Detailed replies are below.

Sec. 1 Introduction: I feel it may help to put some of the material now in section 3.4 already into the introduction. It is not clear to a reader not well acquainted with the topic that the parameter most important for atmospheric implications is actually the diffusivity and that viscosity most often serves only to determine diffusivity and from that characteristic mixing times. In this context I feel the work of Abramson et al. cited on the top of page 6824 need to be singled out and discussed in more detail, since they first measure not viscosity but directly a diffusion constant and second do that also without removal from the aerosol suspension.

We thank the reviewer for your comment and made the following changes to the introduction to address this point.

Recently, the viscosity and the diffusivity of SOM have emerged as important topics (Vaden et al., 2010; Virtanen et al., 2010; Abramson et al., 2013; Hosny et al., 2013; Pajunoja et al., 2013; Power et al., 2013; Renbaum-Wolff et al., 2013; Bateman et al., 2014; Kidd et al., 2014; Wang et al., 2014). These properties influence whether the dynamic interplay between atmospheric particles and gases are confined to the surface region of a particle or alternatively can proceed in the interior (Shiraiwa et al., 2014, 2013b), with potential important consequences for the growth, the reactivity, and ultimately the fate of atmospheric organic particles. Diffusivity of a species and the viscosity of the host matrix are typically quantitatively related to one another, often through the Stokes-Einstein relationship (Lindsay, 2009).

Page 6824, line 13: add Zobrist et al. 2011 (already in the list of references) to the citations as they determine water diffusivity as do Price et al.

We thank the reviewer for the comment. Here we cited only studies that have used secondary organic material to estimate the viscosity and diffusivity. Zobrist et al., an excellent publication, does not involve SOM. The reference does appear, however, in another part of the manuscript.

Page 6825, paragraph starting from line 4: Again I feel the Abramson et al. study should be mentioned here, because it uses suspended aerosol as well and retrieve directly diffusion constants.

We thank the reviewer for the comment. The text is updated as follows (page 6824, line 10):

More recent work, however, has indicated that viscosities are higher and diffusion coefficients are lower than would be consistent with a liquid material (Vaden et al., 2010; Virtanen et al., 2010; Cappa and Wilson, 2011; Perraud et al., 2012; Abramson et al., 2013; Renbaum-Wolff et al., 2013; Kidd et al., 2014; Wang et al., 2014; Price et al., 2015).

Page 6827, line 20: Could you please briefly discuss whether the high concentrations used may lead to SOM not entirely representative of atmospheric SOM?

The high concentrations of SOM are an important consideration when compared with atmospheric SOM. In our previous publications (Shrestha et al. 2013; Shrestha et al. 2015), we discussed the infrared spectrum of alpha-pinene flow tube SOM and chamber SOM. The conclusion is that under our experimental conditions, low mass loading alpha-pinene SOM (such as those from the chamber) and high mass loading SOM (such as those from the flow tube) have similar spectra. There are certainly differences in composition at different mass concentrations, as well as among different experimental approaches to produce SOM, but there is not evidence at this time that these differences affect viscosity, which is an average property. The dependence of viscosity on mass concentration was investigated in a collaboration with Allan Bertram (to be published).

Page 6830, line 23: I would expect a size dependence of the RH at fixed exposure time to elevated RH. This seems not obvious in the data of Fig. 4a. Could you please discuss this?

Yes, a size dependence of merging time is expected. However, the difference becomes observable when only when the sizes change by orders of magnitude, based on our model results. Since the particle sizes vary only from 126.0 nm to 190.0 nm in Fig. 4a, the effect is too small to be discernable in the conducted experiments.

Page 6833, line 22: Please cite the source of the diffusion coefficient of water in alpha-pinene SOM.

The correction of adding the citation of Price et al. 2015 (in press / available on-line) has been made.

Page 6834, line 16: it would be worthwhile to discuss the caveats! May be a short discussion of the results of Power et al.?

We thank the reviewer for your comment. The Stokes-Einstein equation may breakdown when the temperature is close to the glass transition temperature of particle or the gas phase molecules are too small compared with the host matrix molecules. Here we primarily focus on the implication of viscosity for large molecules and at room temperature so these caveats in Power et al. do not apply anymore. Therefore, we updated the text as:

With some limits to applicability (Price et al., 2014), Stokes–Einstein equation relates the diffusion coefficient of a molecule within a host of matrix of viscosity, as follows (Lindsay, 2009):

Figure 4: What are the lines plotted in both panels? If these are fits, please explain. Otherwise write “to guide the eyes” or similar.

We updated the figure caption by adding this to the last sentence of the original caption:

The lines represent empirical fits to the data to guide the eye.

Technical correction: Page 6836: The section starting from line 7: For low and . . . is repeated at the last paragraph on the same page.

The correction is made.

References:

Shrestha, M., Zhang, Y., Ebben, C. J., Martin, S. T., and Geiger, F. M.: Vibrational sum frequency generation spectroscopy of secondary organic material produced by condensational growth from α -pinene ozonolysis, *J. Phys. Chem. A*, 117, 8427–8436, doi:10.1021/jp405065d, 2013.

Renbaum-Wolff, L., Grayson, J. W., Bateman, A. P., Kuwata, M., Sellier, M., Murray, B. J., Shilling, J. E., Martin, S. T., and Bertram, A. K.: Viscosity of α -pinene secondary organic material and implications for particle growth and reactivity, *P. Natl. Acad. Sci. USA*, 110, 8014–8019, doi:10.1073/pnas.1219548110, 2013.

Shrestha, M., Zhang, Upshur, M, Liu, P., Blair, S., Wang, H., Nizkorodov A. S., Thomson J. R. [†], Martin, S. T., and Geiger, F. M.: On Surface Order and Disorder of α -Pinene-Derived Secondary Organic Material, *J. Phys. Chem. A*, 117, 8427–8436, doi:10.1021/jp405065d, 2013.

Price, H. C., Mattsson, J., Zhang, Y., Bertram, A., Davies, J. F., Grayson, J. W., Martin, S. T., O'Sullivan, D., Reid, J. P., Rickards, A. M. J., and Murray, B. J.: Water diffusion in atmospherically relevant alpha-pinene secondary organic material, *Chemical Science*, 10.1039/C5SC00685F, 2015, in press.