Response to comments

Response: We thank the reviewers for thoughtful suggestions and constructive criticism that have helped us improve our manuscript. Below we have detailed responses and resulting edits to all of the reviews' comments. The review comments are listed in italics and black, followed by our responses in normal font and blue. To make it clear, the contents in revised manuscript are presented in quotes and normal font. Reference to line numbers are added to the revised manuscript.

Referee#2:

General Comments: Peng et al present results from coupling an aerodynamic aerosol classifier (AAC) with a single particle aerosol mass spectrometer (SPAMS) to determine individual particle effective density and shape. While this is a worthwhile endeavor, the manuscript misrepresents the prior work on the topic (deriving effective density using a size measurement prior to a single-particle mass spectrometer, which was shown several times in the 2000s). I agree with Johannes Schneider's review and provide additional comments here. A main additional point is that the results need to include propagated measurement error reporting, in the figures and text, for accurate comparisons to theoretical/manufacturer values and to support size-dependent trends, or the lack thereof.

We thank the reviewer for his/her substantial efforts for scrutinizing the manuscript and giving valuable comments and constructive suggestions for improving our manuscript.

1) *As the prior review stated, deriving effective density using a size measurement prior to a single-particle mass spectrometer is not new, and this prior work needs to be discussed in a dedicated added section in the introduction to properly place the current work in context. There are statements, such as those on lines 90, 150-151, and 298-299, that give the impression that this is the first work to measure chemically-resolved particle effective density, and therefore, this phrasing needs to be revised. The lack of*

discussion of this prior work is surprisingly given the author's prior paper, which is cited (Zhang et al. 2016, Sci. China Earth Sci., Measurement of aerosol effective density by single particle mass spectrometry). The introduction of the current manuscript only mentions one prior paper (Moffet and Prather 2005) that derived effective density using an aerosol mass spectrometer (and that work was using scattering signals) and does not discuss prior derivations of shape factors. In addition to Zelenyuk et al. (2006) and Schneider et al. (2006) referenced in the previous review, additional work, not cited in the current paper, includes:

- *Murphy et al. (2004), J. Aerosol Sci., Particle density inferred from simultaneous optical and aerodynamic diameters sorted by composition*

- *Spencer et al. (2007), Environ. Sci. Technol., Simultaneous Measurement of the Effective Density and Chemical Composition of Ambient Aerosol Particles*

- *Slowik et al. (2007), Aerosol Sci. Technol., Measurements of morphology changes in fractal soot particles using coating and denuding experiments: Implications for optical absorption and atmospheric lifetime*

- *Zelenyuk et al. (2008), Analytical Chem., Simultaneous measurements of individual ambient particle size, composition, effective density, and hygroscopicity*

- *Zelenyuk et al. (2008), Environ. Sci. Technol., A new real-time method for determining particles' sphericity and density: Application to secondary organic aerosol formed by ozonolysis of a-pinene*

- *Zelenyuk et al. (2008), J. Phys. Chem. A, "Depth-profiling" and quantitative characterization of the size, composition, shape, density, and morphology of fine particles with SPLAT, a single-particle mass spectrometer*

- *Alexander et al. (2016), Aerosol Sci. Technol., Measurement of size-dependent dynamic shape factors of quartz particles in two flow regimes.*

This may not be a complete list, and therefore, the authors need to do a thorough literature search. In addition to addition to the Introduction, this prior work should also be discussed/compared to in the Results & Discussion. For example, paragraph 2 on page 11 does a good job of comparing to and discussing previous literature, and the manuscript would benefit from this type of comparison and discussion at other points

in the manuscript.

Response: Thanks for your comments and presenting the references about the measurement techniques of the effective density. As suggested, the reference of Moffet and Prather (2005), Moffet et al. (2008), and Zhang et al. (2016a) have been supplemented and summarized in the Introduction. As noted by these studies, the achievements of the ρ_e^{II} are only applicable to the spherical particles. Therefore, we may conclude that it is the first time to achieve the measurement of the ρ_e^{II} and volume equivalent diameter for aspheric particles. Please refer to Lines 87-94:

"Previously, ρ_e^{II} and the real part in the refractive index (n) can be retrieved from a fitting procedure that compares the measured light-scattering intensity of particles (R_{meas}) to the theoretical values ($R_{theory,test}$) calculated by a series of n and ρ_e^{II} values. Moffet and Prather (2005) successfully obtained ρ_e^{II} for spherical particles by single particle mass spectrometry. However, subject to the accuracy of Mie theory for the aspherical particles, dry NaCl and calcium-rich dust particles were failed to fit the $R_{theory,test}$ well to R_{meas} (Moffet et al., 2008). Similarly, Zhang et al. (2016a) failed to simultaneously retrieve ρ_e^{II} and n for $(NH_4)_2SO_4$ and $NaNO_3$ particles."

However, Other references were not included as we focused on the measurement of ρ_e^{II} in the manuscript. We emphasized that three definitions of effective density should be considered as three different properties for the particles in essence. Their final expressions are presented as follows:

$$\rho_e^I = \frac{\rho}{\chi^3} \cdot \left(\frac{C_c(D_{ve})}{C_c(D_m)}\right)^3 \tag{1}$$

$$\rho_e^{II} = \frac{\rho_p}{\chi} \tag{2}$$

$$\rho_e^{III} = \rho \cdot \frac{C_c(D_{ve})}{\chi^2 \cdot C_c(D_m)} \tag{3}$$

where $C_c(D)$ is the Cunningham slip correction factor. The specific difference for three effective densities is shown in the following example: for soot particle with χ of 2.5, ρ of 1.80 g/cm^3 and D_m of 550.0 nm, the values of ρ_e^I, ρ_e^{II}, ρ_e^{III} are calculated to be 0.22, 0.72, and 0.36 g/cm^3, respectively. Such a big gap suggests that it may not be appropriate to compare the three definitions of effective density together, as also suggested by the first reviewer.

2) *The manufacturer reported uncertainties on the PSL sizes need to be reported in the Methods, given the goal of measurement comparison to these values, and then they need to be included when calculating "discrepancies" with the measurements. It is quite possible that the measurement comparison is well within the expected uncertainties. Currently the sizes are stated at 0.X nm accuracy, but my understanding is that the manufactured PSLs are not this monodisperse. For example, a quick look at the manufacturer website suggests that the 203 nm PSLs are provided at +/- 5 nm. Given the direct comparison in the Results to these sizes, the reported accuracy by the manufacturer is key and needs to be reported.*

Response: We agree with the comments. We have added the uncertainties of the PSL sizes determined by Scanning Mobility Particles Sizer (Model 3938, TSI Inc., USA). Please refer to Lines 139-142: "Dried spherical PSL (Nanosphere Size Standards, Duke Scientific Corp., Palo Alto) (ρ_p = 1.055 g/cm^3 and χ = 1.0) with D_{ve} values of 203.0 ± 5.0 nm, 310.0 ± 6.0 nm, 510.0 ± 5.0 nm, and 740.0 ± 6.0 nm were used in the AAC-SPAMS system, and the D_{ve} was verified by Scanning Mobility Particles Sizer (Model 3938, TSI Inc., USA)."

In addition, for the ammonium sulfate, ammonium nitrate, and ambient particles, what is the error in the size selection by the AAC? This is also critical to the method uncertainty. The AAC brochure says that size resolution depends on the sheath to sample flow ratio, so this should also be reported in the methods. Throughout the Results and Discussion text and associated figures, the full measurement uncertainty (that takes into account the width of the size distribution and that it is not monodisperse to the tenth of a nanometer, as implied by reporting values to 0.X nm) needs to be calculated and included in the difference ("discrepancy") calculations. These error bars are particularly needed in Figures 2 and 3 (similar to the inclusion in Figure 4) and in the assessment of any size dependence of effective density. The Figure 4 caption should also state the origin of the error bars shown.

Response: Thanks for the comments. The sample flow was 0.3 lpm in the setup of AAC-

SPAMS, and the value of Size Resolution Parameter (Rs) of the AAC was set as 40 (the Manual of AAC recommends its value ranges from 8 to 80 when the sample flow is 0.3 lpm), which has been added to the Experimental Section. Please refer to Lines 124-125: "The exhaust flow from the AAC was about 0.3 lpm, and the Size Resolution Parameter (Rs) of the AAC was set as 40." We know that the values for the size of PSL particles and the D_{va} measured by SPAMS do not achieve the precision to 0.X nm. However, the size precision can be achieved to be lower than 1 nm when the AAC is applied.

We have revised the significant figures for effective density in the revised manuscript. Considering the precision of the PSL size is less than that of the instrument of AAC, the discrepancy between the measured value (from AAC-SPAMS) and the true value (the size and density of PSL) is used to represent the measurement uncertainty, which is presented in Figure 2 (deviations of size are 0.3%, -0.1%, 0.3% and -0.4%; deviations of density are 4.3%, -5.2%, -5.2%, and 4.3%). The meanings of the solid lines and the data points have been added in the Figure 4 caption, please refer to Lines 466-467: "**Figure 4.** Variation in ρ_e of the eight particle types with D_{ve}. The solid lines represent the standard deviation of the ρ_e and D_{ve} measured from nine rounds, and the data points stand for the average values."

Further, on lines 202-203, it is stated that ": : :in the SPAMS [the] size calibration curve possesses the systematic error." However, this systematic error is not stated or shown (nor is it's origin explained). Further, on Line 206, it is stated that the size-dependent pattern observed is "divergent with the previous studies", but without inclusion of measurement uncertainty, any "pattern" or trend cannot be assessed. Further, often too many decimal places are reported in the manuscript, beyond the appropriate number of significant figures, and this should be evaluated once error is calculated.

Response: Thanks for the comments. The systematic error of size calibration curve has been stated accordingly. Please refer to Lines 224-232: "Figure 3 also shows that the $\rho_{e,me}$ values of the NaNO$_3$ and (NH$_4$)$_2$SO$_4$ particles at four size deviate from their

average values with the maximum of 5.9 % and 4.8%, respectively, which are identical with the deviation for the $\rho_{e,me}$ of PSL particles. These deviations may be derived from the calibration of particle D_{va} from the SPAMS. While the R-square of size calibration curve is 0.999, the curve of exponential function is found to slightly deviate from the data points measured by SPAMS. For example, size calibration function has the deviation of -4.4% and 3.1% from the data points of 310 and 740 nm, respectively. "

3) *In the methods section, Section 2.2 should be separated into laboratory experiments and ambient sampling, for improved clarity. Information should be provided about the diffusion drying tube shown in Figure 1, especially since the water content of the particles is key to the results. The description of the clustering methodology should be moved from the Results to the Methods and expanded. The location and dates of ambient sampling also need to be provided, as well as the actual number of ambient particles measured at each size selected.*

Response: Thanks for the comments and the constructive suggestion. Section 2.2 has been separated into two section, and the location and dates of ambient sampling and the actual number of ambient particles measured at each size selected have been supplemented. Besides, the description of the clustering methodology has been moved from the Results to the Methods, and the corresponding references have been added. Please refer to Lines 138-162:

"2.2 Laboratory experiments

Dried spherical PSL (Nanosphere Size Standards, Duke Scientific Corp., Palo Alto) ($\rho_p = 1.055$ g/cm^3 and $\chi = 1.0$) with D_{ve} values of 203.0 ± 5.0 nm, 310.0 ± 6.0 nm, 510.0 ± 5.0 nm, and 740.0 ± 6.0 nm were used in the AAC-SPAMS system, and the D_{ve} was verified by Scanning Mobility Particles Sizer (Model 3938, TSI Inc., USA). The PSL particles were first classified by AAC, and then their D_{va} values were obtained by the SPAMS. ACC-SPAMS was also applied to the particles of $(NH_4)_2SO_4$ ($\rho_p = 1.77$ g/cm^3) and $NaNO_3$ ($\rho_p = 2.26$ g/cm^3) with D_a values of 250.0 nm, 350.0 nm, 450.0 nm and 550.0 nm.

2.3 Ambient sampling

For field observations, the AAC-SPAMS system was deployed in science and technology enterprise accelerator A2 Block, Guangzhou, China, to characterize the D_{ve}, ρ_e and chemical compositions of aerosol particles. The sampling inlet was hung 2.5 meters from the third floor (~12 m above ground level). Ambient aerosol particles were introduced into the AAC through a 5 m long conductive silicone tube with an inner diameter of 6 mm and a $PM_{2.5}$ cyclone inlet. The overall sampling flow was 3 lpm, and the residence time was approximately 5 seconds. Sampled particles were classified by the AAC as one of four D_a: 250.0 nm, 350.0 nm, 450.0 nm and 550.0 nm. The sampling time for the particles of each D_a was approximately 10 minutes. From July 6th to 8th, 2019, approximately 129,869 ionized particles were obtained from nine rounds of measurement. The sampling details are shown in Table S1. The number of ionized particles with the D_a of 250.0, 350.0, 450.0, and 550.0 nm is about 35,609, 38,374, 31,910, and 23,976, respectively. The sampled ~100,000 particles are first classified by using an adaptive resonance theory neural network (ART-2a) (Song et al., 1999) with a vigilance factor of 0.75, a learning rate of 0.05 and 20 iterations."

The information of the diffusion drying tube and the range of RH at outlet have been added in the Figure 1 caption:

Lines 452-453: "**Figure 1.** Schematic diagram of the AAC-SPAMS system (0.3 lpm). The diffusion drying tube is filled with orange silica gel, which reduces the RH to 5-15%."

4) *Lies 209-211: This sentence is not clear and makes mention of a separate paper being written on the topic of effective density and size-dependent evaluation, but it is not clear why that isn't included here or how it is different.*

Response: This sentence has been deleted in the manuscript. The difference among the three effective density has been illustrated in the Response for the first comment:

"The exact difference for three effective densities is shown in the following example: for soot particle with χ of 2.5, ρ of 1.80 g/cm^3 and D_m of 550.0 nm, the values of $\rho_e{}^I$,

ρ_e^{II}, ρ_e^{III} are calculated to be 0.22, 0.72, and 0.36 g/cm^3, respectively." Besides, according to the result that soot particle with χ of 2.5, ρ of 1.80 g/cm^3 and D_m of 40.0 nm has the ρ_e^{I}, ρ_e^{II}, and ρ_e^{III} of 0.43, 0.72, 0.45 g/cm^3, respectively, it is apparent that the ρ_e^{I} and ρ_e^{III} decrease with increasing particle size while ρ_e^{II} is independent of particle size. The specific reasons are presented in a separate paper mainly dealing with the theoretical bases for three definitions of effective densities, which is not the focus of the present study.

5) *Line 239: By "different", do you mean "wider"?*

Response: Yes, it has been corrected accordingly. Please refer to Lines 262-265: "Besides, the result that the crystallized NaNO$_3$ particles are aspherical is supported by their FWHM values of the D_{va} distributions which are consistent with that of aspherical (NH$_4$)$_2$SO$_4$ but wider than spherical PSL (Figures S1 and S2)."

6) *Lines 255-256: Add a reference to this methods sentence and move to the Methods section.*

Response: Thanks for the comment. Song et al. (1999) has been added accordingly.

7) *Line 281 and Table 1: Note that error should only be reported with 1 significant figure.*

Response: It has been changed accordingly. The values of effective density and size has been modified to 1 significant figure as suggested.

8) *Table 1 caption: State what the error corresponds to here.*

Response: Thanks for the comment. It has been added accordingly. The number after the sign of "±" is its standard deviation, which comes from the nine rounds of measurement. Please refer to Lines 447-449: "**Table 1.** D_{ve} and its standard deviation for the eight particle types at D_a values of 250.0 nm, 350.0 nm, 450.0 nm, and 550.0 nm from nine round measurement."

9) *Figure 1 caption: Add flow rates to the figure to make it more informative.*

Response: Thanks for the comment. It has been added accordingly.

10) *Figure S2b is missing.*

Response: Thanks for the comment. Sorry for this mistake. Fig. S2 do not include the Fig. S2b, so we delete the description of Fig. S2b in the caption. Please refer to Lines 27-28 in Supplement.