

Answers to the review of anonymous Referee #1

We thank Referee #1 for reviewing our manuscript and giving useful suggestions. Below, comments from the referee are given in blue while our answers are given in black. In addition, the new text is marked blue in the revised version of the manuscript.

Review of Pei et al.

This work presents the morphological transformation of soot during condensation of sulfuric acid and limonene SOA. Besides the present work proposes a framework (method) to quantify the parameters of this morphological transformation, i.e. amount of material used for filling voids or diameter growth and fractions of internal/open voids. Overall, this manuscript is well organized and written, the results are clearly presented, and the scientific novelty is significant for the society. However, the MS still needs minor revision and some technical modification. After that, I believe this paper can be published on ACP.

Comments:

1. Abstract: some quantitative result should be added in the abstract rather than general description.

Response: We agree with the referee that some quantitative results should be added.

Action: One sentence “For the largest coating experiments, 6%, 10%, 24% and 58% of condensed material went to filling process, while 94%, 90%, 76% and 42% of condensed material went to growth process for 75 nm, 100 nm, 150 nm and 200 nm soot particles, respectively.” has been added. (See page 1, line 28-31 in the revised manuscript).

2. The expression “framework” is strange.

Response: This is new word in context to morphological transformation of soot aggregate. The methodology of quantifying the filling of voids and growth of mobility diameter with respect to ideal line is referred as “framework”. The framework here is method to quantify. “Framework” seems the most appropriate word in this context.

Action: No change.

3. Line 11: “soot. This work constitutes the first study that quantitatively tracks in-situ microphysical changes in soot morphology”. I don’t think it’s true.

Response: This is a work that had quantified the in-situ morphological transformation of soot aggregate i.e. filling of the voids and growth of particle, nevertheless we agree with the referee that the morphological transformation of soot aggregate has been studied in the previous studies.

Action: We have removed word “first” and modified the sentences wherever appropriate. (See page 2, line 6 and page 18, line 26 in the revised manuscript).

4. Page 1, Line 18 and in the whole manuscript. It is better to use “soot aggregate”, not “soot agglomerate” to keep consistent with most of the literature.

Response: We agree with the referee.

Action: We have changed all “soot agglomerate” to “soot aggregate” in the whole manuscript.

5. Page 1, Line 32: Change “Growth” to “growth”.

Response: We agree with the referee.

Action: Done. (See page 1, line 24 in the revised manuscript).

6. Page 2, Line 1-2: change ‘ ’ to “ ”

Response: We agree with the referee.

Action: Done. (See page 1, line 26 in the revised manuscript).

7. Page 5, Line 27-30: this paragraph describes the steps of the experiments, however, the experiment of soot coated with only SOA is ignored, it should be stated clearly.

Response: We agree with the referee the description of experiment of SOA coated soot should be added.

Action: The whole sentence is changed to “The experimental matrix included four major procedural steps: 1) characterization of the pure soot core; 2) modification of the soot core surface with sulfuric acid and characterization of the modulated soot; 3) modification of soot core surface with SOA and characterization of the modulated soot; 4) modulation of the sulfuric acid modified soot with limonene ozonolysis products and subsequent characterization.” (See page 5, line 24-28 in the revised manuscript).

8. Page 7, Line15-16: Kuwata et al (2012) did not report this 1.26 number but provide a method to calculate the density, this sentence should be checked.

Response: We agree with the referee that the statement is not clear.

Action: the sentence “This value is similar to the organic aerosol density ($1.26 \pm 0.04 \text{ g cm}^{-3}$) estimated from O:C and H:C determined via SP-AMS measurements performed by Kuwata et al. (2012), and the value ($1.3 \pm 0.2 \text{ g cm}^{-3}$) reported by Saathoff et al., (2009). ” has been changed to “In this study,

aerosol mass spectrometer (AMS) was also used in parallel with DMA-APM system. The O:C and H:C determined via AMS measurements were used to estimate the organic aerosol density ($1.26 \pm 0.04 \text{ g cm}^{-3}$) with the method given by Kuwata et al. (2012). The material density of limonene ozonolysis products (1.2 g cm^{-3}) used in this study is similar to the AMS results and the value ($1.3 \pm 0.2 \text{ g cm}^{-3}$) reported by Saathoff et al., (2009).” (See page 7, line 14-18 in the revised manuscript).

9. Page 7, Line 18: change the reference format to Saathoff et al., (2009)

Response: We agree with the referee.

Action: Done. (See page 7, line 17-18 in the revised manuscript).

10. Page 11, Line 6: should be sections 3.3 and 3.4

Response: We agree with the referee.

Action: Done. (See page 11, line 15 in the revised manuscript).

11. Table 3. I suggest that the authors should compare their work with other studies, e.g. Khalizov et al., EST 2013 etc.

Response: We thank for the referee’s suggestion. However, Khalizov et al. (2013) does not present their results of the diameter growth factor (Gfd) as function of coating thickness (Δr_{me}), ($-\Delta r_{me}$ for them cannot be estimated to compare with us) and the maximum coating thickness in this literature is only 6 nm. These two factors make **it difficult to** compare the results of two studies.

Action: No change.

12. Figure 1. The results of SP-AMS and CCN counter were not reported in this paper, should be removed from the figure.

Response: We agree with the referee that SP-AMS and CCN counter are not necessary in this paper.

Action: Done.

13. Figure 6 (a-d): in the abstract, the author state that “In fact, most of the fresh soot particles considered in this study were largely spherical (dynamic shape factor: ~ 1.1)”, however, in this figure, the dynamic shape factors of fresh soot with internal voids are around 1.5-1.9, please check the data consistency. And the black dots in the figure should be changed to blue color as other points without internal voids, or in the legend change “fresh soot” to “fresh soot without internal voids” to make it more clear.

Response: We agree with the referee that the values are not consistent. We have checked the data carefully and we found that in the figures the values are wrong due to a mistake in calculation. The values should be in the range of 1.03-1.08.

Action: Figure 6 has been updated with correct values in the revised manuscript. In addition, the values in Table 1 have also been corrected. The legend for the black dots in Figure 6 has also been changed to “fresh soot without internal voids” according to the referee’s suggestion.

Answers to the review of anonymous Referee #2

We thank Referee #2 for reviewing our manuscript and giving useful suggestions. Below, comments from the referee are given in blue while our answers are given in black. In addition, the new text is marked blue in the revised version of the manuscript.

The authors present data on measurements on the mass equivalent and mobility size of fresh and coated soot particles, which is then interpreted using a framework that can explain the sequential transformations observed. The theoretical treatment is interesting and useful, and the conclusions are for the most part consistent with the data analysis. The subject is very suitable to ACP, and therefore I would suggest publication of the paper. There are some corrections and clarification that need to be made before publication, and I have also a few suggestions to improve readability.

1. Abstract (and conclusion): In the abstract, it is stated that the dynamic shape factor of fresh soot was in most cases ca. 1.1; this is also stated in the conclusions. This is clearly wrong, as none of the values reported e.g. in Table 1 are even close to 1.1. Please correct.

Response: We agree with the referee, the dynamic shape factor in the abstract and conclusions are not same as values in Table 1 and Figure 6. However, after checked the data and calculation carefully, we found that the values in Table 1 and Figure 6 are wrong due to a mistake in calculation. The statement and conclusion on the morphology of fresh soot particles in this study remain valid.

Action: The sentence in the abstract has been changed to “In fact, the dynamic shape factor adjusted for internal voids was close to 1 for the fresh soot particles considered in this study, indicating the particles were largely spherical.” (See page 2, line 2–4 in the revised manuscript). The sentence in the conclusion has been changed to “In fact, the dynamic shape factor adjusted for internal voids (χ_i) was close to 1 for the fresh soot particles considered in this study, indicating the particles were largely spherical.” (See page 18, line 20–21

in the revised manuscript). The values in Table 1 are corrected and Figure 6 is also updated accordingly.

2. Abstract (p2, 111): I'm not sure that it is correct to say that this is the first study to track microphysical changes in situ, as e.g. observations of changes in soot effective density have been made for a long time.

Response: This is a work that had quantified the in-situ morphological transformation of soot aggregate i.e. filling of the voids and growth of particle, nevertheless we agree with the referee that the morphological transformation of soot aggregate has been studied in the previous studies.

Action: We have removed word “first” and modified the sentences wherever appropriate. (See page 2, line 6 and page 18, line 26 in the revised manuscript).

3. p 4, 134: "(ii) volume equivalent inclusive of internal voids": just to clarify; are the internal voids assumed to be part of the particle volume, but external voids are not? If yes, this could be clarified in the explanation of the framework to make following it easier.

Response: We agree with the referee. The internal voids are assumed to be part of the particle volume.

Action: The sentence “(ii) determining the volume equivalent diameter inclusive of internal voids.” has been changed to “(ii) determining the volume equivalent diameter inclusive of unfilled voids.” (See page 4, line 28 in the revised manuscript).

4. p7, eq. 8; when calculating the mass equivalent density of a particle, which density is used? Does this translate also to the mass equivalent coating thickness? This could be useful to indicate, because a person using the

framework will not know which density (effective, sulfuric acid, SOA, etc...) to use.

Response: We agree with the referee, the explanation of the density should be clear. The material density is used to calculate the mass equivalent coating thickness.

Action: In response to address the issue raised by the referee, one sentence “For fresh soot ρ_m is the material density of the soot, whereas for coated particle ρ_m is the average material density over all the components of the particle, which can be calculated from Eq. (4)–(7).” has been added after Eq. (8). (See page 8, line 1-2 in the revised manuscript).

5. p9, 19; I did not fully understand what the difference between the nominal and actual mobility diameters are. They are selected with the same instrumentation and if nothing is done to the aerosol in between, they should be the same? Please clarify.

Response: The nominal mobility diameter is the setting value of the first DMA, whereas the actually mobility diameter is the value measured with the second DMA. These are the digital values by two identical sets of instruments within the instrumental noise/error. So in reality both mean the same.

6. p9, 117: I’m a little bothered by the use of ‘preferentially’ in the paper. If I understand the text correctly, the open voids are filled first (shown by horizontal lines in figs (4), and then the particles start to grow. Are the internal voids filled at all? To my understanding, the internal voids are assumed to be left open (in the framework at least). This could be stated more clearly.

Response: We agree with the referee that open voids are filled first, but the filling of internal voids and particle growth can happen sequentially.

Action: The word “preferentially” appears 3 times in the original version of the manuscript, and the word “preferential” appears once in the original version of the manuscript.

On page 9, line 17 in the original version, the sentence “(i) in the case of SOA, the open voids in the condensed material are preferentially filled prior to the onset of growth” has been changed to “(i) in the case of SOA, the open voids are filled prior to the onset of growth”. (See page 9, line 21 in the revised manuscript).

On page 12, line 29 in the original version, the word “preferentially” has been removed. (See page 13, line 6 in the revised manuscript).

On page 12, line 30 in the original version, the word “preferential” has been removed in the revised version. (See page 13, line 7 in the revised manuscript).

On page 14, line 15 in the original version, the sentence “..., the filling of internal voids occurs preferentially to growth by high surface tension species, ...” has been changed to “..., the filling of internal voids occurs prior to growth by high surface tension species, ...”. (See page 14, line 27 in the revised manuscript).

7. p11, l 27: "The black, red, and green colors in each pie chart represent the mass fraction of black carbon, sulfuric acid, and organics, respectively". How were these mass fractions obtained? Also, this information should be in the caption.

Response: The mass fractions of black carbon, sulfuric acid and organics are calculated from APM measurements. The method to calculate these mass fractions is described in the section 2.2 Data analysis part, and given by Eq. (4)–(6).

Action: In the caption of Figure 4, one sentence “The black, red, and green colors in each pie chart represent the mass fraction of black carbon, sulfuric acid, and organics calculated from Eq. (4)–(6), respectively” has been added.

8. page 12, l25: Move the part starting with 'We assume...' and ending with 'in this work' to the start of the explanation of the framework, as it will clarify the explanation better than here.

Response: We think that it reads quite well here as well.

Action: No change.

9. page 12, line 33: The phrase step-wise filling is often mentioned. I understood that there are basically two steps: void filling, and subsequent growth. Are there more? The collapse of the structure is also mentioned at some point, but this is not shown in Fig. 2. I would suggest that the actual steps are explicitly marked and named in at least one of Figs (4), preferentially all. Also, they should be explained in more detail in the captions.

Response: there are only two basic steps: void filling and particle growth illustrated in the framework. However, in reality, void filling may lead to collapse of the structure (decrease in mobility diameter). We agree with the referee that actual steps should be marked and named in Figure 4.

Action: To give an example, actual steps including voiding filling, particle growth and collapse are marked by arrows and named in Figure (4d). The explanation of the purple lines "Purple lines parallel to the ideal sphere growth line (dashed black) represent growth of the particle diameter; purple lines parallel to the x -axis represent filling of voids; purple lines with negative slope indicates a combination of void filling and collapse of the soot particle." has been added in the caption.

10. Page 15, line 20-22: . . . "This may introduce some shift in the mapping of the mass and mobility size, leading to overestimation of Δr_{me} ." I don't really understand how the continuous growth causes a shift in the measured mobility

or mass; please clarify this. Also, is there a reason why the soot differs so much in the internal/open void properties between the present and literature studies in Table 3?

Response: In smog chamber experiments, SOA composition is changing continuously because it is constantly evolving from reactions and aging of SOA. In fact, SOA condensed on soot is not the same in any two measurements. So we think that the continuous growth of soot in smog chamber may be different for two consecutive points since it took about 20-30 min to acquire two measurement points. In other words, during the measurement the particles in the environmental chamber were evolving and there are several factors that can cause the differences between this study and literature studies:

1) The coating devices and time scales were different: in this study the coating device was laminar flow reactor and the residence time was 4.8 min while in the literature studies the coating device was a collapsible environmental chamber and the time for each their experiment was several hours.

2) The soot was different: in this study the soot was generated from a premixed-diffusion flame and denuded with a thermos-denuder at 400 °C, while in the literature studies the soot was generated from a Santoro-type laminar diffusion burner without thermo-denuder.

3) The condensed materials were different: in this study the coating materials were two types: sulfuric acid and limonene ozonolysis SOA, while in the literature studies the condensed materials were only SOA: toluene OH oxidation products in Qiu et al. (2012), and m-xylene OH oxidation products in Guo et al. (2016).

11. Conclusions, p. 17, l21: '...this is the first study that considers the effect of coatings with two chemical components'. Is there any conclusions drawn on the effect of the different components, and which properties cause these differences? I could not find these, and as this is not the main purpose of the paper, maybe this sentence could be changed.

Response: We agree with the referee that the statement on the effect of coatings with two chemical components is not clear.

Action: The sentence “To the best of our knowledge, this is the first study that considers the effect of coatings with two chemical components (i.e., sulfuric acid and SOA) on soot morphology.” has been removed. (See page 18, line 9 in the revised manuscript).

Changes according to co-authors' suggestions

We also change some text in the manuscript according to our co-authors' suggestions, and they are marked in blue in the revised manuscript with makeup. The page numbers and line numbers are according to the revised version with makeup.

Page 1, line 4: In “Joakim H. Pagels”, “H.” is removed.

Page 1, line 19: “discovered” is changed to “hypothesize”.

Page 1, line 31-33: “We also used the framework to estimate the fraction of internal voids and open voids. This information was then used to derive the volume equivalent diameter of the soot aggregate containing internal voids and to calculate the *in-situ* dynamic shape factor” is changed to “We also used the framework to estimate the fraction of internal voids and open voids. This information was then used to estimate the volume equivalent diameter of the soot aggregate containing internal voids and to calculate the dynamic shape factor, accounting for internal voids.”

Page 2, line 2: “*in-situ*” is removed.

Page 2, line 2-4: “In fact, most of the fresh soot particles considered in this study were largely spherical (dynamic shape factor: 1.03–1.08).” is changed to “In fact, the dynamic shape factor adjusted for internal voids was close to 1 for

the fresh soot particles considered in this study, indicating the particles were largely spherical.”

Page 2, line 7-8: “This work constitutes the first study that quantitatively track *in-situ* microphysical changes in soot morphology,...” is change to “In this work we quantitatively tracked *in-situ* microphysical changes in soot morphology,...”

Page 2, line 27: “..., aged hygroscopic soot is more efficiently deposited in the lungs” is changed to “..., aged hygroscopic soot has an altered deposition in the lungs”.

Page 3, line 6: “..., and proportionality constant, respectively.” is change to “..., and a proportionality constant, respectively.”

Page 8, line 4-5: “For fresh soot ρ_m is the material density of the soot, whereas for coated particle ρ_m is the average material density over all the components of the particle, which can be calculated from Eq. (4)–(7).” is changed to “For fresh soot ρ_m is the inherent material density of the soot, whereas for coated particle ρ_m is the average inherent material density over all the components of the particle, which can be calculated from Eq. (4)–(7).”

Page 8, line 5-7: Sentence “It should be pointed out that this definition of the mass equivalent diameter is identical to the definition of volume equivalent diameter used by McMurry et al. (2002) and Park et al. (2003).” is added.

Page 8, line 13-18: The text is changed to “

The dynamic shape factor χ can be calculated from the measured mobility diameter D_p and the mass equivalent diameter D_{me} (Baron and Willeke, 2001):

$$\chi = \frac{D_p C_{me}}{D_{me} C_p}, \quad (10)$$

where C_{me} and C_p are the Cunningham slip correction factors for particles with diameters D_{me} and D_p , respectively. The dynamic shape factor is derived directly from Stokes’ law. It is the ratio of the drag force exerted on the irregular particle divided by the drag force exerted on its mass equivalent sphere, when travelling at the same speed.”

Page 8, line 18-20: “In situ experimental determination of D_{ve} is not currently possible and, hence, soot aggregates free of internal voids are typically assumed, leading to $D_{ve} = D_{me}$.” is removed.

Page 8, line 22-23: “The void space fraction (F_{vs}), i.e., volume of voids/total volume of particles derived from the mobility diameter, is calculated from the D_{me} and D_p of fresh and coated soot:” is changed to “The void space fraction (F_{vs}), i.e., volume of voids/total volume of particles derived from the mobility

diameter, is estimated from the D_{me} and D_p of fresh and coated soot (Baron and Willeke, 2001; Zhang et al., 2016):”

Page 9, line 26: “in the condensed material” is removed.

Page 10, line 4-6: the text “

Then $D_{ve,i}$ is used to calculate the dynamic shape factor with internal voids (χ_i):

$$\chi_i = \frac{D_p C_{ve,i}}{D_{ve,i} C_p}, \quad (20)$$

where $C_{ve,i}$ is corresponding Cunningham slip correction factors for $D_{ve,i}$.” is added.

Page 10, line 23-24: “However, compared with previous studies, our quantification considers internal voids (which in fact results in significantly smaller χ) and therefore yields more accurate χ (see section 3.4).” is removed.

Page 10, line 28 – page 11, line 1: “This value is consistent with that reported for fresh soot particles from a diffusion propane burner” is changed to “This value is consistent with aggregates reported for fresh soot particles from a diffusion propane burner”

Page 11, line 22: “fractality ” is changed to “porosity”.

Page 11, line 24-25: “In previous studies, χ was calculated based on the assumption that internal voids were absent from the soot aggregate. This assumption yields $D_{me} = D_{ve}$. In this work, D_{ve} increases whereas χ decreases with the occurrence of internal voids (see sections 3.3 and 3.4 for the experimentally determined open-void fractions and relevant discussions).” is changed to “In previous studies, χ was calculated based on $D_{me} = D_{ve}$. In this work, D_{ve} increases whereas χ_i decreases when we attempt to adjust for internal voids (see sections 3.3 and 3.4 for the experimentally determined open-void fractions and relevant discussions).

Page 11, line 32 – page 12, line 1: “S, M, L” is changed to “small, medium, large” and they are all changed in the whole manuscript.

Page 15, line 18: “200 nm soot particle with a mass...” is changed to “200 nm soot particles with a mass...”

Page 15, line 33-34: “Detailed estimates associated with each step of filling and shrinkage of the 200 nm soot are provided in Table S2 of the supplement.” is changed to “Detailed estimation associated with each step of filling and shrinkage of the 200 nm soot is provided in Table S2 of the supplement.”

Page 16, line 8: “...leading to overestimation of Δr_{me} .” is changed to “...leading to either underestimation or overestimation of Δr_{me} .”

Page 16, line 22-23: “However, as previously stated, our experimental results show that internal voids dominate the total void space in all four cases.” is changed to “However, as previously stated, our experimental results when interpreted with the new framework suggest that internal voids dominate the total void space in all four cases.”

Page 16, line 24-26: “Therefore, the χ values obtained based on the *no internal voids* assumption differ significantly (see Fig. 6) from the experimentally determined values obtained in this study.” is changed to “Therefore, the χ values obtained based on the *no internal voids* assumption (χ_n) differ significantly (see Fig. 6) from the values where we attempted to adjust for internal voids (χ_i).”

Page 16, line 28-31: “This assumption neglects the *in-situ* morphology of the soot aggregate, and stipulates (based on the notion of a void-less sphere) that the equivalent volume is equal to the sum of the all primary spherules. These findings highlight the serious shortcomings of the assumption that $D_{ve} = D_{me}$ and the implications for atmospheric surface processes that are considered critical for modeling-based studies.” is changed to “This assumption stipulates (based on the notion of a void-less sphere) that the equivalent volume is equal to the sum of all the primary spherules. These findings have implications for atmospheric surface processes that are considered critical for modeling-based studies.”

Page 16, line 31 – page 17, line 3”: “As shown in Fig. 6(a)–(d), a significant amount of material is condensed on the soot particles, but a perfect sphere remains elusive. For e.g., the thickness of the coating on the 75 nm particle is at least two times larger than the initial mobility diameter, but χ still deviates from unity (Exp. 15). This results from the fact that χ is estimated (Eq. 10; $D_{ve} = D_{me}$) based on the assumption that the internal voids measured in our experiment are all open voids.” is changed to “As shown in Fig. 6(a)–(d), a significant amount of material is condensed on the soot particles, but a perfect sphere remains elusive. For e.g., the thickness of the coating on the 75 nm particle is at least two times larger than the initial mobility diameter, but χ_n still deviates from unity (Exp. 15). This results from the fact that χ_n is calculated (Eq. 10) based on the assumption that the voids measured in our experiment are all open voids.”

Page 17, line 5-9: “The χ values determined in previous studies (see Table S4) based on the *no internal voids* assumption appear to be consistent with each other for the wrong reason. In reality, and as confirmed in this study, the occurrence of internal voids in a soot aggregate is unavoidable. Therefore, we suggest that the framework introduced in this work should be developed using an experimental setup, i.e., a flow tube integrated with a DMA-APM. This setup will yield *in-situ* D_{ve} associated with the morphological characteristics of soot and the transformation of these characteristics upon the condensation of material.” is removed.

Page 17, line 9-18: “Our framework highlights that the high values of the dynamic shape factor found at high coating thicknesses can not only be caused by truly non-spherical particles (for example a few chains of the soot core sticking out from a spherical droplet) but in addition internal porosity in the soot core that blocks full penetration of the condensed species. Thus, internal porosity causes uncertainty when judging the particle shape with conventional approaches. The main uncertainty in the new framework comes from the determination of F_{vs} and F_i . For example, when assigning a volume fraction of voids based on mobility measurements and when dividing F_{vs} into internal (F_i) and open void space based on the growth curves. In addition, when interpreting the data using our framework one finds that the low values of Dfm as well as size-dependent effective density do not always indicate soot aggregates have an open-structure, but instead compact soot cores with increasing internal porosity can also have these features and match the mass-mobility data.” is added.

Page 17, line 23: “lines” is changed to “curves”.

Page 17, line 24-25: “The method of calculating the ideal growth curve is described in detail in the supplement.” is added. The detail information is added in the supplement accordingly.

Page 18, line 26: “on” is changed to “due to”.

Page 19, line 2-4: “The dynamic shape is also calculated from the parameters derived by the framework. The dynamic shape factor estimated from traditional assumptions and methods differs significantly from the value determined in this study.” is changed to “The dynamic shape factor calculations where we attempted to account for internal voids (χ_i) is also calculated from the parameters derived by the framework. The dynamic shape factor estimated from traditional assumptions and methods (χ_n) differs significantly from the value determined in this study.”

Page 19, line 4-6: “In fact, most of the fresh soot particles considered in this study are largely spherical, with a dynamic shape factor of 1.03–1.08.” is changed to “In fact, the dynamic shape factor adjusted for internal voids (χ_i) was close to 1 for the fresh soot particles considered in this study, indicating the particles were largely spherical”

Page 19, line 11: “represents first study that” is removed.

Several new references are added in the references list.

Morphological transformation of soot: investigation of microphysical processes during the condensation of sulfuric acid and limonene ozonolysis product vapors

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Abstract.

The morphological transformation of soot particles via condensation of low-volatility materials constitutes a dominant atmospheric process with serious implications for the optical and hygroscopic properties, and atmospheric lifetime of the soot. We consider the morphological transformation of soot [aggregates](#) under the influence of condensation of vapors of sulfuric acid, and/or limonene ozonolysis products. This influence was systematically investigated using a Differential Mobility Analyzer-Aerosol Particle Mass Analyzer (DMA-APM) and the Tandem DMA techniques integrated with a laminar flow-tube system. We ~~hypothesize discovered~~ that the morphology transformation of soot results (in general) from a two-step process, i.e., (i) filling of void space within the [aggregate](#); (ii) growth of the particle diameter. Initially, the transformation was dominated by the filling process followed by growth, which led to the accumulation of sufficient material that exerted surface forces, which eventually facilitating further filling. The filling of void space was constrained by the initial morphology of the fresh soot as well as the nature and the amount of condensed material. This process continued in several sequential steps until all void space within the soot [aggregate](#) was filled. And then “[growth](#)” of a spherical particle continued as long as vapors condensed on it. We developed a framework for quantifying the microphysical transformation of soot upon the condensation of various materials. This framework used experimental data and the hypothesis of “ideal sphere growth” and void filling to quantify the distribution of condensed materials in the complementary filling and growth processes. Using this framework, we quantified the percentage of material consumed by these processes at each step of the transformation. [For the largest coating experiments, 6%, 10%, 24% and 58% of condensed material went to filling process, while 94%, 90%, 76% and 42% of condensed material went to growth process for 75 nm, 100 nm, 150 nm and 200 nm soot particles, respectively.](#) We also used the framework to estimate the fraction of internal voids and open voids. This information was then used to ~~estimate derive~~ the volume equivalent diameter of the soot [aggregate](#) containing internal voids and to calculate the ~~in-situ~~ dynamic shape factor, [accounting for internal voids](#). The dynamic shape factor estimated based on

the traditional assumption (of no internal voids) differed significantly from the value obtained in this study. Internal voids are accounted for in the experimentally derived *in-situ* dynamic shape factor determined in the present study. In fact, the dynamic shape factor adjusted for internal voids was close to 1 for the fresh soot particles considered in this study, indicating the particles were largely spherical. ~~In fact, most of the fresh soot particles considered in this study were largely spherical (dynamic shape factor: 1.03–1.08).~~ The effective density was strongly correlated with the morphological transformation responses to the condensed material on the soot particle and the resultant effective density was determined by the (i) nature of the condensed material; (ii) morphology and size of the fresh soot. In this work we constitutes the first study that quantitatively tracked *in-situ* microphysical changes in soot morphology, providing details of both fresh and coated soot particles at each step of the transformation. This framework can be applied to model development with significant implications for quantifying the morphological transformation (from the viewpoint of hygroscopic and optical properties) of soot in the atmosphere.

1 Introduction

Soot containing black carbon (BC) produced from incomplete combustion of fossil-fuel or biomass is ubiquitous in the atmosphere, and represents a major constituent of atmospheric aerosols (Bond et al., 2013). Through direct radiative forcing, soot influences the climate significantly as it efficiently absorbs light in the visible and infrared spectral ranges.

Once emitted into the atmosphere, soot particles undergo morphological transformations due to several ageing processes. Soot ageing includes adsorption and condensation of semi-volatile vapors, coagulation with pre-existing aerosol particles, heterogeneous reactions with atmospheric gaseous species, and in-cloud processing (Khalizov et al., 2009). The physical and chemical properties of soot particles change considerably during these ageing processes. For example, exposure to sulfuric acid changes the morphology, enhances the absorption and scattering, and increases the hygroscopicity of fresh soot particles (Zhang and Zhang, 2005; Zhang et al., 2008). The cloud forming properties of soot can be altered, and climate forcing can be influenced (albeit indirectly), by coating the soot with soluble material. For example, atmospheric ageing of coated soot enhances the hygroscopicity of the coatings and, hence, aged soot particles can act as efficient cloud condensation nuclei (CCN) or ice nuclei (IN) (Ammann et al., 1998; Henning et al., 2012). Transformation from fresh hydrophobic soot to processed hygroscopic soot can also have adverse health effects as, compared with hydrophobic fresh soot, aged hygroscopic soot has an altered is more efficiently depositioned in the lungs (Löndahl et al. 2008).

Soot particles are emitted as complex aggregates. Their morphology and life-span in the atmosphere are directly correlated with the atmospheric processing (e.g., the type and the amount of material condensed on the aggregate). The mass mobility exponent (D_{fm}) is an indirect measure of the morphology of irregularly shaped aggregated particles (DeCarlo et al., 2004). The DMA-APM technique characterizes the properties of fresh or coated soot aggregates by performing simultaneous

measurements with a differential mobility analyzer (DMA) and an aerosol particle mass analyzer (APM) (McMurry et al., 2002). With this technique, the mobility diameter and mass of the same [aggregate](#) particles are accurately measured, and the mass mobility exponent is determined through fitting of the mass-mobility relationship. The mass mobility exponent, Dfm , is defined as:

$$5 \quad Dfm = \frac{\ln(m_p) - \ln(k)}{\ln(D_p)}, \quad (1)$$

where D_p , m_p , and k are the particle mobility diameter, particle mass, and [a](#) proportionality constant, respectively.

The effective density of a particle, ρ_{eff} , can also be determined from simultaneous measurements of the mass and mobility diameter, and is given as follows:

$$10 \quad \rho_{eff} = \frac{6m_p}{\pi D_p^3}, \quad (2)$$

where m_p is the particle mass and D_p is the mobility diameter.

A Dfm of 3.0 is obtained for spherical particles, whereas values of 2.2–2.4 are typically obtained for fresh diesel soot (Park et al. 2003). This range of values is indicative of an open-structure aggregate. Schneider et al. (2006) found that particles
 15 resulting from biomass burning have variable Dfm values: for dry beech fuel $Dfm = 2.1$, whereas for humid oak fuel Dfm was close to 3.0. Fresh soot from various sources, such as a diesel engine, diffusion-type burner, and premixed-type burner, have effective densities of 0.2–1.2 g cm⁻³, which typically decrease with increasing mobility diameter (Ghazi et al., 2013; Rissler et al., 2013).

20 Previous studies (Zhang et al., 2008; Weingartner et al., 1995) have found that the mobility diameter of fresh hydrophobic soot below water saturation (relative humidity < 100%) undergoes a relatively small amount of hygroscopic growth. This indicates that, at sub-saturation, water vapor has little influence on the soot morphology. However, soot particles will become hydrophilic if water-soluble compounds, such as sulfuric acid or organics condense on the surface, and then collapse into a spherical shape when the relative humidity (RH) is increased (Zhang et al., 2008; Pagels et al., 2009). The effective
 25 density of coated and annealed soot increases, consistent with restructuring of the soot cores after they acquire sufficient fractions of coating material (Cross et al., 2010; Qiu et al., 2012; Saathoff et al., 2003; Pagels et al., 2009). The extent of restructuring depends on the production conditions of the soot, as well as on the mass fraction and type of the coating material. Carbon soot aggregates produced from spark discharge collapse to relatively compact shapes at sub-saturation, whereas diesel soot undergoes limited restructuring (Weingartner et al., 1997). Different dicarboxylic acids have different
 30 effects on soot restructuring. Exposure to glutaric acid (C₅ low RH_{deliquescence}) leads to significant collapse of the soot cores, whereas condensation of succinic acid (C₄, high RH_{deliquescence}) has no influence on the restructuring (Xue et al., 2009). Secondary organic aerosol (SOA) produced from OH-initiated oxidation of both toluene and isoprene results in an increase in the effective density and a significant decrease in the dynamic shape factor of the cores (Qiu et al., 2012; Khalizov et al.,

2013). However, the effect of limonene SOA on soot ageing has yet to be studied, despite the fact that limonene comprises up to 10% of the total global monoterpene emissions (Geron et al., 2000; Guenther et al., 2012) and has very high potential for SOA formation. Limonene is efficiently oxidized to SOA with little or no carbon loss, generating water-soluble products (Pathak et al., 2012) due to two different unsaturated bonds in the molecule: an endocyclic tri-substituted double bond and an
5 exocyclic terminal double bond. In this work, we determine the effect of limonene ozonolysis products on soot morphology.

Sulfuric acid – formed during the combustion processes, condenses on soot and provides active acidic surfaces for the condensation of semi-volatile SOA. The acid-catalyzed SOA reactions can enhance SOA formation significantly, as shown in laboratory experiments (Jang et al. 2002). However, soot – SOA interactions mediated by surface acidity have barely been
10 investigated. For e.g., the effect of an SOA-added acidified soot surface on the morphology, density, and, hence, the lifetime of soot in the atmosphere as well as the radiative properties remains unexplored.

Condensation of such low-volatility materials on soot particles leads to morphological transformation of these particles with serious implications for the corresponding optical and hygroscopic properties, and atmospheric lifetime. Nevertheless, many
15 aspects of this transformation (including the mechanism of void-space filling within fractal soot and the restructuring and *in-situ* growth upon condensation of different materials) remain unclear. The correlation (i.e., mutual dependence and/or sequential dependence) or lack thereof between these processes must also be clarified. To date, these microphysical aerosol processes are neither described in current models nor fundamentally studied and quantified. Therefore, major knowledge gaps remain, thereby hindering the development of robust modeling tools for improved climate predictions.

20 To address these issues, a study of chemical and physical processes encompassing the interaction of SOA with soot on the acidic surfaces is performed using a flow-tube reactor at the University of Gothenburg, Sweden. In this study, soot processing is investigated using controlled condensation of sulfuric acid and SOA onto a laboratory-generated propane flame soot. We perform direct measurements of the change in mobility diameter and mass upon processing, using the TDMA and
25 DMA-APM techniques. The mass-mobility relationship is then used to calculate the mass mobility exponent, effective density, and dynamic shape factor of soot subjected to processing of atmospheric relevance. Subsequently, the results are compared with those of previous studies. A framework is developed for quantifying the morphological state and subsequent transformation of soot, i.e., the utilization of material for filling and growth upon the condensation of material. Using this framework, a method is derived for (i) quantifying the fraction of internal voids and open voids in the soot [aggregate](#), and (ii)
30 determining the volume equivalent diameter inclusive of [unfilled](#) voids.

2 Experimental methods

Soot particles emitted from a premixed-diffusion propane flame soot generator with and without coatings were studied. The coating processes were systematically performed in a temperature and RH-controlled laminar flow tube as shown in Fig. 1. The key instruments used included an APM, two DMAs, and two condensation particle counters (CPCs). A schematic of the experimental setup is shown in Fig. 1.

2.1 Soot generation

Laboratory-scale soot-SOA interaction process experiments were performed using a versatile propane premixed-diffusion flame soot generator built, in-house, to produce sub-micron soot particles with desired particle size and concentration. Different flame conditions were realized by regulating the fuel to air equivalence ratios. Details of the flame selection and flame conditions are provided elsewhere (Pei et al, 2017).

The soot from the propane flame generator was dried with a silica gel diffusion drier, and a Thermo-Denuder (TD) was then used to remove each of the co-produced primary organic components, as shown in Fig. 1. The TD was maintained at 400 °C and the particle residence time within the TD was ~1.6 min. Further downstream, NO_x was removed using a NO_x denuder filled with charcoal granite (Activated Charcoal Powder USP, Spectrum Chemical Mfg. Corp., USA). The poly-dispersed pure soot cores were charged by a bipolar charger (⁶³Ni) and then selected using the first DMA (DMA1, model 3081, TSI Inc., Shoreview, MN, USA, aerosol flow rate 0.4 L min⁻¹, and sheath flow rate 6.0 L min⁻¹) for size-resolved modulation and subsequent characterization experiments.

2.2 Soot modification

Soot particles were modulated using the experimental setup of the Tandem Differential Mobility Analyzer (TDMA) with the integrated flow-tube system and then characterized using the APM, DMAs, and CPC, as shown in Fig. 1. The size selected mono-disperse soot core surface was modified by sulfuric acid coatings using a cylindrical glass mixing chamber (length: 47 cm, diameter: 10 cm) equipped with a temperature-regulated bath system. The modified soot particles were then further modulated by SOA generated via limonene ozonolysis in a low NO_x, dark laminar flow tube (flow rate: 1.52 L min⁻¹ and effective particle residence: 4.8 min at 25 °C and regulated RH).

Four nominal sizes of soot core, i.e., 75, 100, 150, and 200 nm, were selected using DMA1. The experimental matrix included four major procedural steps: 1) characterization of the pure soot core; 2) modification of the soot core surface with sulfuric acid and characterization of the modulated soot; 3) modification of soot core surface with SOA and characterization

of the modulated soot; 4) modulation of the sulfuric acid modified soot with limonene ozonolysis products and subsequent characterization.

The acid-induced surface modifications were performed at three different temperatures namely, 1 °C (small=S), 5 °C (medium=M), and 25 °C (large=L), using a temperature-regulated bath system. In the SOA modulation steps, the limonene concentrations in the flow tube were regulated using flowing zero air over limonene in a diffusion vial submersed in a temperature-regulated bath system (Jonsson et al., 2008). The limonene mixing ratios in the flow-tube (56 ppb, 73 ppb, 138 ppb) were precisely regulated by setting the temperatures of the limonene vial bath system to 1 °C (small=S), 5 °C (medium=M), and 15 °C (large=L) at a constant zero air flow rate (0.002 L min⁻¹). Ozone was generated by passing zero air (Ultra Zero Air Generator GT 3000, LNI SCHMIDLIN AG) through a UV-lamp unit (SOG-3, UVP). The ozone concentration used in the experiments was set to a constant value of 1432 µg m⁻³ (~730 ppb) and monitored using a UV photometric ozone analyzer (model 49C, Thermo Environmental Instruments Inc.). A low constant RH (5±1%) was maintained in all cases. The nucleation of limonene ozonolysis products may happen during the modification process; however, since the homogeneous nucleated SOA particles did not have a charged soot core, they cannot be selected by DMA2 and will not influence the soot characterization results.

For (i) pure soot core characterization, the modulation steps involving sulfuric acid and limonene SOA were all bypassed (see Fig. 1), (ii) determining the effect of sulfuric acid on soot mobility and morphological properties, only the modulation steps involving limonene SOA were bypassed (by turning off the ozone production through the UV-lamp power supply; see Table S1 of the supplementary information for the experimental matrix). (iii) determining the effect of pure limonene SOA on soot mobility and morphological properties, the modulation steps involving sulfuric acid were bypassed

2.3 Aerosol characterization

2.3.1 DMA+CPC for the particle-size number distributions

The post modulation peak diameters of the mono-disperse soot cores were scanned using a combination of a DMA (DMA2, Vienna type, length 280 mm, inner/outer radius 25.0/33.3 mm, aerosol flow rate 2.25 L min⁻¹, and sheath flow rate 10.0 L min⁻¹) and a condensation particle counter (CPC – model 3775, TSI Inc., Shoreview, MN, USA, flow rate 0.3 L min⁻¹), which served as a scanning mobility particle sizer (SMPS).

2.3.2 DMA-APM for the size-resolved particle mass

After DMA2, the mass of the mono-disperse particle population was measured using a series combination of an APM (model APM-3600, Kanomax) and a CPC (model 3775, TSI Inc., Shoreview, MN, USA, flow rate: 0.3 L min⁻¹, see Fig. 1).

The APM consists of two concentric cylinders rotating at the same angular speed. A voltage was applied over the cylinders and the particles introduced in the gap between these cylinders experienced a centrifugal force. The APM transmitted only those particles with a specific mass at which the electric force is equal to the centrifugal force. These particles were then counted with a CPC (Rissler et al., 2013). The DMA-APM system was calibrated using two sizes of polystyrene latex spheres (Duke Scientific Corp., USA), in accordance with previously described methodology (McMurry et al., 2002). Moreover, the mass sensitivity of multiply charged particles was determined and for all soot particle sizes, the mass was overestimated by <5% (see supplementary information).

2.4 Data analysis

The particle diameter growth factor, Gfd , is calculated from:

$$10 \quad Gfd = \frac{D_p}{D_{p,0}}, \quad (3)$$

where D_p and $D_{p,0}$ are the mobility diameter of particles at a given reaction time and the mobility diameter of the fresh soot particles, respectively.

The particle effective density ρ_{eff} can be calculated from Eq. (2). The particle organic mass fraction fm_{org} is determined from: $(m_p - m_{SA} - m_0)/m_p$, and the particle sulfuric acid mass fraction fm_{SA} is determined as m_{SA}/m_p , where m_p , m_{SA} and m_0 are mass of coated particle, mass of sulfuric acid coating and mass of fresh soot, respectively. Similarly, the material density ρ_m is calculated from the material density of the soot (ρ_{soot} : 1.77 g cm⁻³), organic coating (ρ_{org}), and sulfuric acid (ρ_{SA}) if volumetric additivity is assumed. The material density of limonene ozonolysis products (ρ_{org} : 1.20 g cm⁻³) measured by Chen et al. (2010) is used in this study. In this study, aerosol mass spectrometer (AMS) was also used in parallel with DMA-APM system. The O:C and H:C determined via AMS measurements were used to estimate the organic aerosol density (1.26±0.04 g cm⁻³) with the method given by Kuwata et al. (2012). The material density of limonene ozonolysis products (1.20 g cm⁻³) used in this study is similar to the AMS results and the value (1.3±0.2 g cm⁻³) reported by Saathoff et al., (2009). The material density of sulfuric acid (sulfuric acid-water mixture) at 5±1% RH (ρ_{SA} : 1.84 g cm⁻³) is estimated using the same method employed by Pagels et al. (2009). The material density ρ_m is calculated from:

$$25 \quad m_{SA} = m_{p,soot+SA} - m_0, \quad (4)$$

$$fm_{SA} = \frac{m_{SA}}{m_p}, \quad (5)$$

$$fm_{org} = \frac{m_p - m_{SA} - m_0}{m_p}, \quad (6)$$

$$\frac{1}{\rho_m} = \frac{fm_{org}}{\rho_{org}} + \frac{fm_{SA}}{\rho_{SA}} + \frac{1 - fm_{org} - fm_{SA}}{\rho_{soot}}, \quad (7)$$

The mass equivalent diameter D_{me} corresponds to a spherical particle of the same mass, and can be calculated from the particle mass m_p and the material density ρ_m :

$$D_{me} = \sqrt[3]{\frac{6m_p}{\pi\rho_m}}, \quad (8)$$

For fresh soot ρ_m is the inherent material density of the soot, whereas for coated particle ρ_m is the average inherent material density over all the components of the particle, which can be calculated from Eq. (4)–(7). It should be pointed out that this definition of the mass equivalent diameter is identical to the definition of volume equivalent diameter used by McMurry et al. (2002) and Park et al. (2003).

The change in particle D_{me} is expressed as the mass equivalent coating thickness Δr_{me} :

$$\Delta r_{me} = \frac{D_{me} - D_{me,0}}{2}, \quad (9)$$

where $D_{me,0}$ and D_{me} are the mass equivalent diameters of the fresh and the coated soot particles, respectively.

The dynamic shape factor χ can be calculated from the measured mobility diameter D_p and the volumemass equivalent diameter D_{mve} (Baron and Willeke, 2001):

$$\chi = \frac{D_p C_{mve}}{D_{me} C_p}, \quad (10)$$

where C_{mve} and C_p are the Cunningham slip correction factors for particles with diameters D_{me} and D_p , respectively. The dynamic shape factor is derived directly from Stokes' law. It is the ratio of the drag force exerted on the irregular particle divided by the drag force exerted on its massvolume equivalent sphere, when travelling at the same speed. In situ experimental determination of D_{ve} is not currently possible and, hence, soot aggregates free of internal voids are typically assumed, leading to $D_{ve} = D_{me}$.

The void space fraction (F_{vs}), i.e., volume of voids/total volume of particles derived from the mobility diameter, is estimated/calculated from the D_{me} and D_p of fresh and coated soot (Baron and Willeke, 2001; Zhang et al., 2016):

$$F_{vs} = 1 - \frac{D_{me}^3}{D_p^3}, \quad (11)$$

In this study, the model developed by Sorensen (2011) is used to describe the relation among the particle mobility diameter D_p , primary particle (soot spherules) diameter d_{pp} , and number of primary particles (soot spherules) in a soot aggregate (N). We assume that the primary particles of soot aggregates are in point contact and the material density of these particles is the same as that (1.77 g cm^{-3}) of the soot.

$$m_p = N \cdot \frac{\pi}{6} \rho_m d_{pp}^3, \quad (12)$$

$$D_p = d_{pp} N^x, N < 1000, \quad (13)$$

where $x = 1/Dfm = 0.46$ assuming a Dfm of 2.17 for the soot [aggregate](#). In the original Sorensen model, a fixed exponent x was used for $N < 100$. However, Rissler et al. (2013) suggested that the formula should also be used for N values of up to 5 1000.

2.5 Framework for quantifying the morphological transformation

A framework was developed for quantifying the state of the morphological transformation of soot, i.e., the utilization of material for filling and growth, as shown in Fig. 2. Fig. 2(a) shows the particle diameter growth factor (Gfd) as a function of the coating thickness Δr_{me} associated with each measurement point. The ideal growth line, denoted by a black solid line, describes condensation of material on a perfect incompressible solid sphere with the same initial mobility diameter and mass as a fresh soot particle. We hypothesize that when material condenses on the soot [aggregate](#), the growth process will be described by Gfd parallel to the ideal growth line, while void filling will be described by a line parallel to the x -axis. The coating thickness for void filling ($\Delta r_{me,f}$) and the coating thickness for particle growth ($\Delta r_{me,g}$) are indicated by the red arrow (parallel to the x -axis) and the green arrow (parallel to the ideal growth curve), respectively. From this framework, the 15 fraction of void space filled ($F_{vs,f}$), volumes of material utilized for void filling (V_f) and diameter growth (V_g), and the percentages of material utilized for filling (P_f) and growth (P_g) can be derived as follows (based on the assumption of a concentric core shell structure; see Fig. 2(b) for illustration):

$$F_{vs,f} = \frac{(D_{me,0} + 2\Delta r_{me,f})^3 - D_{me,0}^3}{D_p^3 F_{vs}}, \quad (14)$$

$$V_f = \frac{\pi}{6} [(D_{me,0} + 2\Delta r_{me,f})^3 - D_{me,0}^3], \quad (15)$$

$$20 \quad V_g = \frac{\pi}{6} [(D_{me,0} + 2\Delta r_{me,f} + 2\Delta r_{me,g})^3 - (D_{me,0} + 2\Delta r_{me,f})^3], \quad (16)$$

$$P_f = \frac{V_f}{V_f + V_g}, \quad (17)$$

$$P_g = \frac{V_g}{V_f + V_g}, \quad (18)$$

During the experiment, the soot undergoes step-wise morphological transformation (see section 3.3 for details). The fraction 25 of internal voids (F_i) and the fraction of open voids (F_o) in the soot [aggregate](#) are determined based on the following hypotheses: (i) in the case of SOA, the open voids ~~in the condensed material~~ are [preferentially](#) filled prior to the onset of

growth, and (ii) at the onset of growth, F_o is equal to the fraction of void space filled ($F_{vs,p}$), whereas $F_i = 1 - F_o$. The volume equivalent diameter including internal voids ($D_{ve,i}$) is then given as:

$$D_{ve,i} = \sqrt[3]{D_{me}^3 + D_p^3 F_{vs} F_i}, \quad (19)$$

Then $D_{ve,i}$ is used to calculate the dynamic shape factor with internal voids (χ_i):

$$\chi_i = \frac{D_p C_{ve,i}}{D_{ve,i} C_p} \quad (20)$$

where $C_{ve,i}$ is corresponding Cunningham slip correction factors for $D_{ve,i}$.

3 Results

3.1 Fresh soot properties

As previously mentioned, fresh pure soot is obtained by heating the soot particles in the TD at 400 °C to remove co-produced organics from the soot generator. For the soot transformation study, four fresh pure soot particle sizes with nominal mobility diameters (D_p) of 75, 100, 150, and 200 nm are selected using DMA1. The corresponding actual mobility diameters (actual D_p) are scanned using DMA2 and CPC, as shown in Fig. 1. The D_p , mass equivalent diameter (D_{me}), mass (m_p), effective density (ρ_{eff}), and the dynamic shape factor (χ) of the particles are listed in Table 1. As the table shows, the final measured D_p of the modified soot differs only ~5% from the instrumental accuracy of the DMA1 and the SMPS (DMA2+CPC) system. The calculated D_{me} is smaller than the D_p corresponding to each size, i.e., D_{me} of 57.1, 70.8, 95.3, and 116.2 nm are obtained for D_p of 75, 100, 150, and 200 nm, respectively. This suggests that the soot particle contains significant fractions of void space (F_{vs}). In fact, the estimated fraction of void space within a fresh soot particle (listed in Table 1) is fairly large, e.g., F_{vs} values of 58%, 63%, 72%, and 78% are obtained for D_p of 75, 100, 150, and 200 nm, respectively. These void fractions account for both internal and external voids (see section 3.4). However, the corresponding dynamic shape factor (χ), a parameter describing the sphericity of the particle (see Table 1), is estimated based on the assumption of no internal voids. The value of χ increases from 1.66 to 2.29 with increasing (from 75 to 200 nm) D_p . This indicates, as reported in previous studies (Xue et al., 2009; Khalizov et al., 2013), that the shape irregularity of the particle increases with increasing mobility diameter. ~~However, compared with previous studies, our quantification considers internal voids (which in fact results in significantly smaller χ) and therefore yields more accurate χ (see section 3.4).~~

The morphological structure of the soot **aggregate** may also be described via the mass-mobility exponent (Dfm), which characterizes the primary particles (spherules) and describes their arrangement within the **aggregate**. Averaged over all four sizes, i.e., 75, 100, 150, and 200 nm, a Dfm of 2.28 is derived by fitting the actual D_p and the soot particle mass. This value is

consistent with ~~aggregates that~~ reported for fresh soot particles from a diffusion propane burner (Pagels et al., 2009). We used the D_{fm} of pure BC particles in Eq. (11) and Eq. (12) to determine the size of the primary spherules (d_{pp}), and a value of ~ 28 nm is obtained for all four sizes of the soot aggregates. The d_{pp} reported in previous studies vary significantly and are typically lower than the value obtained in this study. For e.g., Pagels et al. (2009) and Zhang et al. (2008) obtained a d_{pp} of ~ 15 nm via TEM image analysis. Similarly, Rissler et al. (2013) obtained, via TEM analysis, values of 24, 27, 28, 11, and 13 nm, for particles (geometric mean diameter: 50 nm) associated with a heavy-duty transient diesel engine, heavy-duty idling diesel engine, light-duty idling diesel engine, candle, and propane flame soot, respectively. Our d_{pp} (i.e., 28 nm) is similar to that obtained from field measurements performed by Rissler et al. (2014), indicating that the soot aggregates considered in this study are similar to real-world soot particles. According to the Sorensen model, the d_{pp} determines the void fraction in the aggregate. Therefore, quantifying the d_{pp} is essential for a complete description of the morphological state of the soot aggregate.

Generally, comparison with previous studies is difficult, owing to the use of different fresh soot material as the substrate for subsequent soot transformation studies. The properties reported in selected studies are summarized in Table S4. As the table shows, fresh soot particles with similar mobility diameter ($D_p \sim 100$ nm) have similar D_{fm} (2.14–2.28), but widely varying (15 nm–45 nm) d_{pp} . This indicates that the soot aggregates are formed through a similar coagulation process after the nascent primary spherules are formed in the flame. The results reported in the literature can be classified into two groups: (1) Pagels et al. (2009), Xue et al. (2009), Qiu et al. (2012), Khalizov et al. (2013), and Peng et al. (2016) generated similar soot with χ of ~ 2.2 and d_{pp} of 15–21 nm; (2) Guo et al. (2016) and Ghazi and Olfert (2013) generated similar soot with relatively compact morphology characterized by $\chi = 1.5$ and $d_{pp} = 45$ nm. The compactness of the soot considered in this study ($\chi = 1.81$ and $d_{pp} = 28$ nm) represents an intermediate of these two groups. This results from the fact that, for any given soot core mobility diameter, the porosity/fractality of the soot aggregate increases with decreasing d_{pp} . In previous studies, χ was calculated based on ~~the assumption that internal voids were absent from the soot aggregate. This assumption yields~~ $D_{me} = D_{ve}$. In this work, D_{ve} increases whereas χ_i decreases ~~when we attempt to adjust for the occurrence of~~ internal voids (see sections 3.3 and 3.4 for the experimentally determined open-void fractions and relevant discussions).

3.2 Formation of limonene ozonolysis SOA

Limonene SOA was formed on the soot surface regulated by VOC, ozone and sulfuric acid concentrations in the experiments. In general, compared with those formed from the reactions of VOC and ozone, significantly higher amounts of SOA formed when the reactions occurred on the acid-coated soot surfaces. The levels of acidity on the surface play an important role in this formation. Fig. 3 shows the masses of different levels of sulfuric acid and SOA coatings associated with a 200 nm soot core. The amounts of sulfuric acid and limonene SOA coatings on a soot particle are classified as small (S), medium (M), and large (L). The mixed coating experiments cover the full matrix, i.e., BC coated with each of the ~~Ssmall, mediumM,~~ and

~~large~~ amounts of sulfuric acid is also co-coated with ~~small~~S, ~~medium~~M, and ~~large~~ amounts of limonene SOA. Soot cores of other sizes (75, 100, and 150 nm) exhibit similar trends to those observed for the 200 nm soot. Acidity-induced enhancement of the SOA mass is attributed to acid-catalyzed heterogeneous reaction mechanisms (such as hemiacetal and acetal formation) of carbonyls in SOA, polymerization, and aldol condensation (Jang et al., 2002). The mass of SOA formed on the BC particle surface under ~~large~~ SOA and ~~large~~ sulfuric conditions was significantly higher than the total mass of ~~large~~ SOA formed under ~~large~~ sulfuric acid only and on the acid-free surface. Therefore, we achieved various particle coating thicknesses, which allowed a thorough investigation of the morphological transformation of the BC particle.

3.3 Growth of the particle mobility diameter

The mobility diameter growth factor (Gfd) implies that the morphological transformation of soot ~~aggregates~~ results from condensation of the material. Fig. 4(a)–(d) shows Gfd , associated with initial fresh soot mobility diameters of 75, 100, 150, and 200 nm, as a function of the mass equivalent coating thickness (Δr_{me}). The Gfd values are measured for the full experimental matrix described above. In Fig. 4, the ideal growth curve is denoted by the black dashed line and the pie chart denoting each data point shows the chemical composition of fresh and processed soot particles. The black, red, and green colors in each pie chart represent the mass fraction of black carbon, sulfuric acid, and organics, respectively. We hypothesize that the morphological transformation of soot particles result from the: (i) filling of void space within a fractal soot ~~aggregate~~; (ii) growth of mobility diameter identical to that of the ideal sphere (parallel to black dashed line); (iii) rearrangement of primary spherules, i.e., collapse, within a fractal soot ~~aggregate~~ due to surface forces exerted by the condensed material. Condensational growth of the material will increase the mobility size and mass of the particles. Adding material to the void space of the soot structure will increase the mass, but the mobility size will remain the same or decrease due to collapse. We have observed all three effects (see Fig. 4). The morphological transformation of the soot fraction results from a combination of two or more of these processes and, when expressed as the Gfd , exhibits a strong particle size dependence. The morphological properties associated with the four sizes of fresh soot are shown in Table 1. Furthermore, the Gfd associated with different coatings are illustrated by purple lines and the trends are summarized as follows, the: (i) line parallel to the ideal sphere growth line (dashed) indicates that all material added was utilized for growth of the particle diameter; (ii) line parallel to the x -axis indicates that all condensed material was utilized for filling the void space within a fractal soot ~~aggregate~~; (iii) negative slope indicates a combination of void space filling and collapse of the soot particle.

The soot structure of fresh soot particles with diameter and mass of 75 nm and 0.17 fg (Exp. 1), respectively, is relatively resistant to collapse. The major morphological transformation occurs sequentially in a step-wise manner, with filling of void space (shown by the solid purple line parallel to the x -axis) and growth of the diameter (solid purple line parallel to the black dashed line) as a function of Δr_{me} (mass equivalent coating thickness; see Fig. 4(a)). When the heaviest coating is applied to the 75 nm soot ~~aggregate~~ with ~~large~~ sulfuric acid (0.26 fg) + ~~large~~ SOA (2.37 fg) (Exp. 15), 94% of the total volume of

the condensed material is utilized for diameter growth (see Fig. 4(a)). Only 6% is utilized for filling the void space, but this 6% has filled 97% of the void space within the soot particle (Table 2). The morphological evolution of the soot appears to be independent of the type of condensed material. In other words, in the present study, pure sulfuric acid, pure SOA, and acidity-mediated SOA participate indiscriminately in the process of void filling and growth of the 75 nm soot particle. In the

5 (i) ~~smallS~~ and ~~mediumM~~ pure sulfuric acid experiments (Exp. 4, 0.02 fg and Exp. 8, 0.03 fg, respectively), 93% and 100%, respectively, of the condensed sulfuric acid are utilized for filling. (ii) ~~largeL~~ pure sulfuric acid experiment (Exp. 12, 0.26 fg), 23% of the condensed material is utilized for void filling, resulting in the filling of 25% of the voids. (iii) ~~smallS~~ and ~~mediumM~~ pure SOA (Exp. 2, 0.08 fg and Exp. 3, 0.11 fg, respectively), only 23% and 35% of the condensed material are utilized for void filling, resulting in 12% and 26%, respectively, of filled voids. These results show that the growth of

10 material on the soot plays a dominant role in soot transformation. We assume that the microphysical structure of the soot ~~aggregate~~ considered in this study contains mainly two types of voids (as outlined by DeCarlo et al. (2004)) namely, (i) internal voids, i.e., space shielded by soot primary spherules, and (ii) open voids, i.e., space open to the atmosphere (shown in Fig. 2(c)). We assume that both types of voids lie within a hypothetical sphere of mobility diameter. Furthermore, we interpret our data in light of the knowledge that the open voids will be ~~preferentially~~ filled over the internal voids, due to the

15 shielding of primary spherules. This ~~preferential~~-filling characterizes the microphysical transformation of the soot considered in this work. The space within the internal voids is probably bottlenecked due to the narrow opening, thereby preventing the entry of material except for large masses (5–15 times of the soot particle mass) of the condensed material (as observed in Exp.11 and Exp. 13–15). These occurrences seem to control the step-wise filling and subsequent growth process, which proceed until the voids are all filled. The indiscriminate behavior of pure sulfuric acid and pure SOA in the morphological

20 transformation of 75 nm soot particles is attributed to the same growth and filling patterns (see Fig. 4(a)). This suggests that most of the void space is occupied by internal voids, as evidenced by the filling of only 10% of voids prior to the onset of sharp growth. The percentage of voids filled and the growth of the particle diameter are quantified (see Table S2) at each step shown in Fig. 4(a). Thus, we have quantified the state of morphological transformation (from beginning to end) as a function of the amount and type of material condensed on the soot ~~aggregate~~.

25 We also consider 100 nm soot consisting of particles with mass of 0.33 fg. Upon condensation of the material, the major morphological transformation occurs sequentially in a step-wise fashion, i.e., filling of void space and growth of diameter, as previously described for the 75 nm soot (see Fig. 4(b)). When condensed ~~largeL~~ sulfuric acid (0.34 fg) + ~~largeL~~ SOA (1.50 fg) is applied (Exp. 31), 90% of the total volume of the condensed material is utilized for diameter growth. The remaining 10%

30 is utilized for filling, resulting in filling of 44% of the void space. In contrast to that observed for the 75 nm soot, the response on the morphological transformation of the 100 nm fresh soot exhibits a strong dependence on the type of material condensed. Most of the volume (54%) of the ~~largeL~~ pure sulfuric acid (Exp. 28) is utilized for initial filling (up to 10 nm $A_{r_{me}}$ filled 30% of the void space). For ~~largeL~~ pure SOA (Exp. 19), only 17% of void filling occurs, but the diameter growth is greater (80% of material utilized for growth and only 20% for filling) than in the case of ~~largeL~~ pure sulfuric acid. This

eventually leads to two different pathways of morphological transformation of the soot particle, leading to a hysteresis of transformation (see Fig. 4(b) and Table S2 of the supplementary information). This hysteresis constitutes a response to the nature of condensing material and the type of microphysical void space (internal voids or open voids) within the soot particle. For e.g., the condensation of [mediumM](#) (Exp. 24) followed by [largeL](#) (Exp. 28) sulfuric acid on pure soot lead to a void filling of 30%, due to the higher surface tension relative to that associated with [largeL](#) SOA. This higher tension yields efficient filling of some (21%) of the internal voids prior to the onset of major particle growth. Similar forces and similar filling (26%) can be achieved with additional [largeL](#) SOA and [smallS](#) sulfuric acid (Exp. 23) on the soot by increasing the amount of material. The type of growth and void filling associated with the hysteresis suggest that the 100 nm soot [aggregate](#) contains mainly internal voids, which require a considerable amount of condensable material to fill. For example, only 44% (maximum) of void space is filled when almost five times the soot core mass consisting of acidity-mediated SOA (1.84 fg) is condensed (Exp. 31). This suggests that, in the case of pure SOA, the internal void structure inhibits void-space filling (growth begins at 10% of void-space filling). However, 30% of void filling is achieved for [largeL](#) sulfuric acid (0.34 fg, Exp. 28). Morphological transformation from the [largeL](#) sulfuric acid experiment (Exp. 28) to [largeL](#) sulfuric acid + [largeL](#) SOA experiment (Exp. 31), is dominated by growth of the diameter (the extent of this growth ranges from 7% to 59% relative to void filling, i.e., 30% ([largeL](#) sulfuric acid) to 44% ([largeL](#) sulfuric acid + L SOA)). Owing to the surface tension of sulfuric acid, its vapors can efficiently enter the narrow spaces of internal voids within the soot [aggregate](#), thereby resulting in filling prior to the onset of growth. However, in the case of SOA, growth begins with complete filling of the open voids, indicating that the initial diameter growth (leading to 10% of void filling) determined the open-void fraction (i.e., 10%).

In the case of 150 nm fresh soot with a mass of 0.75 fg, 76% of the total volume of the condensed material is utilized for diameter growth. In contrast, 24% is utilized for filling when a mixture of [largeL](#) sulfuric acid + [largeL](#) SOA (Exp. 46) is condensed, leading to 39% of void-space filling and 30% diameter growth. The major morphological transformation occurs sequentially in a step-wise manner (see Fig. 4(c)), i.e., with sequential filling and growth of the diameter. Furthermore, the response to the nature of the material and the hysteresis of the transformation differ significantly from those of the 100 nm particle. For example, 2% growth is initially achieved in three experiments namely, [mediumM](#) sulfuric acid (Exp. 39), [largeL](#) sulfuric acid (Exp. 43), and [smallS](#) SOA (Exp. 33). Void filling of 3%, 25%, and 9%, respectively, are achieved for these experiments. Increasing the amount of SOA, e.g., in Exp. 39 ([mediumM](#) sulfuric acid) and Exp. 43 ([largeL](#) sulfuric acid), yields a significant change in the response to morphological transformation pathways, although similar growth is achieved. In other words, additional [largeL](#) SOA in Exp. 39 (Exp. 42) leads to 13% growth and 29% void filling, while additional [smallS](#) SOA to [largeL](#) sulfuric acid in Exp. 43 (Exp. 44) leads to 11% growth and 42% void filling. This leads to hysteresis of the transformation, as shown in Fig. 4(c). The process of void filling and particle growth is quantified at each step shown in Fig. 4(c) (see Table S2 of the supplement). The same level of growth (i.e., 2%) occurs in these three experiments irrespective of the nature of the condensed material and the percentage of the volume of the condensed material that is utilized for void filling (39%, 81%, and 70% for Exp. 39, Exp. 43, and Exp. 33, respectively). This suggests that most of the

initial filling occurs for open voids. When open voids are filled completely, the filling of internal voids occurs [preferentially prior](#) to growth by high surface tension species, such as pure sulfuric acid (e.g., 56 Nm^{-1}). SOA with low surface tension (e.g., $25\text{--}30 \text{ Nm}^{-1}$) will, however, lead to growth. Compared with that required for growth of the diameter (high surface energy barriers), a smaller surface area is required for the filling of voids (lower energy barriers). Sulfuric acid tends to fill even the internal voids prior to growth of the diameter, but SOA fills these voids only after growth has begun. In other words, the ability of sulfuric acid to fill some internal voids prior to growth can be attributed to its high surface tension and low vapor pressure. Owing to these characteristics, the relatively low surface energy barriers of the internal voids are easily overcome. The filling of open voids will largely be completed when SOA growth begins. This hypothesis is verified by quantifying the fraction of internal to open voids within the boundary of the hypothetical sphere of mobility diameter. As in the case of the 75 nm and 100 nm soot [aggregates](#), the 150 nm soot contains a smaller fraction (i.e., 10%) of open voids than internal voids. All (100%) of these voids are filled, whereas only 33% of the internal voids (constituting 90% of all voids in the soot) is filled during the heaviest coating experiment (Exp. 46). The morphological transformation process of the 150 nm soot differs (e.g., from the viewpoint of hysteresis) from that of the 75 nm and 100 nm [aggregates](#). For e.g., during the heaviest coating experiments, 6%, 10%, and 24% of the condensed material are utilized for filling in the 75 nm, 100 nm, and 150 nm soot, respectively. However, in terms of absolute fractions, condensational growth still dominated over void filling for both sulfuric acid and SOA.

200 nm soot particles with a mass of 1.46 fg is also considered. When coated with ~~large~~ sulfuric acid (0.68 fg) + ~~large~~ SOA (2.00 fg) (Exp. 62), 42% of the total volume of condensed material is utilized for diameter growth and 58% is used for filling. This filling resulted in 41% of the void space filled. The percentage of condensed material utilized for filling increases significantly when the soot size is increased from 75 nm to 200 nm, confirming that more void space occurs in the larger size soot. This is consistent with the estimated F_{vs} result. As anticipated, the major morphological transformation results from sequential step-wise filling and growth of the 200 nm soot particle. Furthermore, the response to the nature of the condensed material and the hysteresis of the transformation are similar to those of the 150 nm soot particle. Internal [re-](#)arrangement of primary spherules within the hypothetical sphere of mobility diameter that shrinks or collapses ($Gfd < 1$) is also possible. Upon the addition of ~~small~~/~~medium~~/~~large~~ sulfuric acid (Exp. 51, Exp. 55, Exp. 59) and S SOA (Exp. 48) to the 200 nm soot [aggregates](#), indiscriminate shrinkage occurs, owing to the rearrangement of primary spherules. The fraction of open voids may increase with this rearrangement and shrinkage of 4% and 2% occur for ~~large~~ sulfuric acid (Exp. 59) and SOA (Exp. 48). The initial fraction of open voids (10%) is filled by ~~small~~ SOA (Exp. 48), and additional (7%) open voids are created with subsequent condensation of the material (Exp. 48). These additional voids are filled during Exp. 56 and Exp. 57 (as indicated by negligible growth of the diameter). However, compared with SOA, sulfuric acid is more efficient at filling the internal voids when more material is condensed (Exp. 59–62) and 31% of these voids (constituting a void fraction of 83%) is filled. This filling accounts for 26% of the total void space. Detailed [estimations](#) associated with each step of filling and shrinkage of the 200 nm soot ~~isare~~ provided in Table S2 of the supplement.

Previous studies considering the morphological transformation of soot using similar techniques are also evaluated with the framework described above (Guo et al. 2016; Qiu et al. 2012). Fig. 5 shows the Gfd as a function of Δr_{me} for the 100 nm soot transformation measured in a smog chamber by Guo et al. (2016) and Qiu et al. (2012). The major difference between those experiments and the experiments employed in this study is that a flow tube (rather than a smog chamber) is used in the present work. The smog chamber allows dynamic particle growth, i.e., particle properties including mobility diameter and mass are measured in 40-min intervals while particles are continuously growing. This may introduce some shift in the mapping of the mass and mobility size, leading to [either underestimation or overestimation](#) of Δr_{me} . Nevertheless, the framework provides a fairly good depiction of the features associated with the morphological transformation (i.e., filling and growth) of their soot. These features are consistent with the ideal sphere growth theory. Our framework reveals that their soot is composed mainly of open voids (84–95%) as indicated by their growth curve, where the growth line is parallel to the x -axis (no growth). In their studies, growth and filling occur sequentially, but over very short time intervals, indicating that internal voids are relatively easy to fill. This highlights the major differences (see Table 3) between the present study and previous studies. These results show that the framework developed in this study is quite capable of evaluating the mass and mobility data required for interpreting the morphological transformation of soot of various sizes.

3.4 Dynamic shape factor

The dynamic shape factor, χ , is an important parameter used to represent the shape of both fresh and coated soot particles. $\chi = 1$ and $\chi > 1$ correspond to perfectly spherical particles and irregularly shaped particles, respectively. Fig. 6(a)–(d) shows χ as a function of the coating thickness Δr_{me} for four different fresh soot sizes and the same soot cores coated with either pure sulfuric acid, pure SOA or acidity-mediated SOA. These are calculated from Eq. (10) assuming that the soot aggregate is free of internal voids. However, as previously stated, our experimental results [when interpreted with the new framework suggests how](#) that internal voids dominate the total void space in all four cases. Void fractions of 88%, 91%, 89%, and 83% are obtained for the 75 nm, 100 nm, 150 nm, and 200 nm soot, respectively. Therefore, the χ values obtained based on the *no internal voids* assumption (χ_i) differ significantly (see Fig. 6) from the [values where we attempted to adjust-correct for internal voids \(\$\chi_i\$ \)-experimentally determined values-obtained in this study.](#)

This assumption [neglects the *in situ* morphology of the soot aggregate, and](#) stipulates (based on the notion of a void-less sphere) that the equivalent volume is equal to the sum of [all the all](#)-primary spherules. These findings [have highlight the serious shortcomings of the assumption that \$D_{ve} = D_{me}\$ and the](#) implications for atmospheric surface processes that are considered critical for modeling-based studies. As shown in Fig. 6(a)–(d), a significant amount of material is condensed on the soot particles, but a perfect sphere remains elusive. For e.g., the thickness of the coating on the 75 nm particle is at least

two times larger than the initial mobility diameter, but χ_u still deviates from unity (Exp. 15). This results from the fact that χ_u is ~~calculated~~^{estimated} (Eq. 10; $D_{ve}=D_{me}$) based on the assumption that the ~~internal~~ voids measured in our experiment are all open voids.

~~The χ values determined in previous studies (see Table S4) based on the *no internal voids* assumption appear to be consistent with each other for the wrong reason. In reality, and as confirmed in this study, the occurrence of internal voids in a soot aggregate is unavoidable. Therefore, we suggest that the framework introduced in this work should be developed using an experimental setup, i.e., a flow tube integrated with a DMA-APM. This setup will yield *in-situ* D_{ve} associated with the morphological characteristics of soot and the transformation of these characteristics upon the condensation of material. Our framework highlights that the high values of the dynamic shape factor found at high coating thicknesses can not only be caused by truly non-spherical particles (for example a few chains of the soot core sticking out from a spherical droplet) but in addition internal porosity in the soot core that blocks full penetration of the condensed species. Thus, internal porosity causes uncertainty when judging the particle shape with conventional approaches. The main uncertainty in the new framework comes from the determination of F_{vs} and F_i . For example, when assigning a volume fraction of voids based on mobility measurements and when dividing F_{vs} into internal (F_i) and open (F_o) void space based on the growth curves. In addition, when interpreting the data using our framework one finds ~~suggests that~~ that the low values of Dfm as well as size-dependent effective density do not always indicate soot aggregates have an open-structure, but instead compact ~~spherical~~ soot cores with increasing internal porosity can also have these features ~~thers~~ and match the mass-mobility data.~~

20 3.5 Effective density

Fig. 7 (a)–(d) shows the effective density (ρ_{eff}) as a function of the coating thickness (Δr_{me}) for four different fresh soot sizes. Ideal growth ~~curves lines~~ of effective density correspond to growth of material on a perfect sphere with the same mass and mobility diameter as fresh soot grown by either pure sulfuric acid or pure SOA. The coating thickness of the ideal sphere is based on the corresponding mass-equivalent fresh soot. The method of calculating the ideal growth curve is described in detail in the supplement.

As described in section 3.3, the morphological transformation (mostly the growth) responds indiscriminately to the addition of pure sulfuric acid and pure SOA to the 75 nm soot. The same response occurs for the effective density of the coated particles. For example, the pure sulfuric acid points are consistent with the ideal growth curve shown in Fig. 7(a) and most of the SOA and acidity-mediated SOA points lie on the ideal growth curve of SOA. These observations support our description of the morphological transformation of the 75 nm soot (see section 3.3). Unlike those associated with the 75 nm soot, the sulfuric acid as well as the SOA and acidity mediated SOA points of the 100 nm soot lie slightly above the respective ideal

growth curves of pure sulfuric acid and SOA (see Fig. 7(b)). This results from the fact that more material is utilized for void filling (than for diameter growth), leading to an increase in the particle mass without diameter growth (see section 3.3 for details of the 100 nm particle). The increase in mass results in a sharp increase in ρ_{eff} . However, when particle growth occurs, ρ_{eff} increases only modestly and follows (for the most part) the ideal curve. In the case of acidity-mediated SOA, most of the points lie between the ideal growth curves of two pure substances, indicative of combined sulfuric acid and SOA growth as well as filling. The 100 nm particle transformation is still dominated by growth and, hence, points from the acidity-mediated SOA heavy coating experiment are close to $\sim 1.1 \text{ g m}^{-3}$ (see section 3.3), which approaches the pure SOA ideal curve. For the 150 nm soot, ~~large~~ sulfuric acid points lie above the sulfuric acid ideal growth curve, which describes the response to filling. ~~Large~~ sulfuric acid + ~~small~~/~~medium~~/~~large~~ SOA points result from filling and growth, as discussed in section 3.3. However, the corresponding ρ_{eff} values evolve in a complex manner as the materials (pure soot, pure sulfuric acid, and SOA) in the system have different material densities and mass fractions. The ρ_{eff} increases moderately in these experiments when coatings from ~~small~~ to ~~large~~ SOA are applied. Other points, representing mainly the growth-dominant transformation of the 150 nm soot via SOA condensation, lie close to the SOA ideal growth curve, as shown in Fig. 7(c). In the 200 nm soot, most of the initially condensed material is utilized for filling and growth is negligible. Therefore, points from the ~~large~~ sulfuric acid experiment lie above the sulfuric acid ideal growth curve. Similarly, several points from the SOA coating experiment lie above the SOA ideal growth curve. The occurrence of points above the curves is consistent with morphological transformation linked to the filling of voids. The morphological transformation occurring during the heavy acidity-mediated SOA coating experiments (Exp. 60–62) is also dominated by the filling of voids. This filling yields increased ρ_{eff} for points well above the SOA ideal growth curve and around the sulfuric acid ideal growth curve. In each case, ρ_{eff} results from the microphysical transformation of the soot ~~aggregate~~ and changes in this value are consistent with the findings described in section 3.3.

4 Conclusion

Soot particles generated from a propane flame were aged via condensation of sulfuric acid, limonene ozonolysis products or a mixture of both, in a laminar flow tube system. ~~To the best of our knowledge, this is the first study that considers the effect of coatings with two chemical components (i.e., sulfuric acid and SOA) on soot morphology.~~ A framework is developed for quantifying the microphysical transformation of soot ~~due to~~ the condensation of material. This framework utilizes experimental data and the hypothesis of ideal sphere growth and filling of voids to quantify the distribution of condensed materials during a two-step process consisting of diameter growth and void filling. Using this framework, we quantify the percentage of material that is utilized for particle growth and void filling at each step. In the initial stages, filling is the dominant process followed by some growth, which leads to the accumulation of sufficient material. This material exerts a large surface force that facilitates further filling. The process continues in several sequential steps depending on the initial morphology of the fresh soot and the nature as well as the amount of condensed material. Using the same framework, we

estimate the fraction of internal voids and open voids and use this information to derive the volume equivalent diameter of a soot aggregate containing internal voids. The *in-situ* dynamic shape factor [calculations where we attempted to account for internal voids \(\$\chi_i\$ \)](#) is also calculated from the parameters derived by the framework. The dynamic shape factor estimated from traditional assumptions and methods (χ_i) differs significantly from the value determined in this study. [In fact, the dynamic shape factor adjusted for internal voids \(\$\chi_i\$ \) was close to 1 for the fresh soot particles considered in this study, indicating the particles were largely spherical](#) ~~In fact, most of the fresh soot particles considered in this study are largely spherical, with a dynamic shape factor of 1.03–1.08.~~ The effective density is strongly correlated with the morphological transformational responses to the condensed material on the soot particle and the resultant effective density is determined by the (i) nature of the condensed material and (ii) morphology and size of the fresh soot.

This work ~~represents first study that~~ quantifies (*in-situ*) microphysical changes in soot morphology, providing details of both the fresh and coated soot particles. The employed framework may be useful for developing a model that determines the morphological transformation and microphysical properties (including hygroscopic and optical properties) of soot in the atmosphere.

15 Acknowledgement

This work was supported by the Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning (FORMAS: Project No. 214-2011-1183), Modelling the Regional and Global Earth system (MERGE) and Climate, Biodiversity and Ecosystem services (ClimBEco).

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Table 1. Mobility diameter, mass equivalent diameter, mass, effective density, dynamic shape factor, void space fraction, primary particle size, and number of primary particles of different sizes of fresh soot particles (errors: standard deviation of all the values).

Nominal D_p (nm)	Actual D_p (nm)	D_{me} (nm)	mass (fg)	ρ_{eff} (g cm ⁻³)	$\chi^{\#}$ without internal voids	χ with internal voids	F_{vs} (%)	d_{pp} (nm)	N
75	76.0±1.4	57.1±0.2	0.17±0.01	0.77±0.08	1.66±0.03	1.04	58	27.9	8
100	99.0±1.1	70.8±1.2	0.33±0.02	0.65±0.07	1.81±0.04	1.03	63	28.5	15
150	146.2±1.4	95.3±1.1	0.77±0.03	0.48±0.04	2.10±0.03	1.04	72	27.7	39
200	193.3±3.4	116.2±4.2	1.46±0.16	0.39±0.09	2.29±0.09	1.08	78	28.0	72

[#] these dynamic shape factors were calculated assuming that internal voids were absent from the soot [aggregate](#)

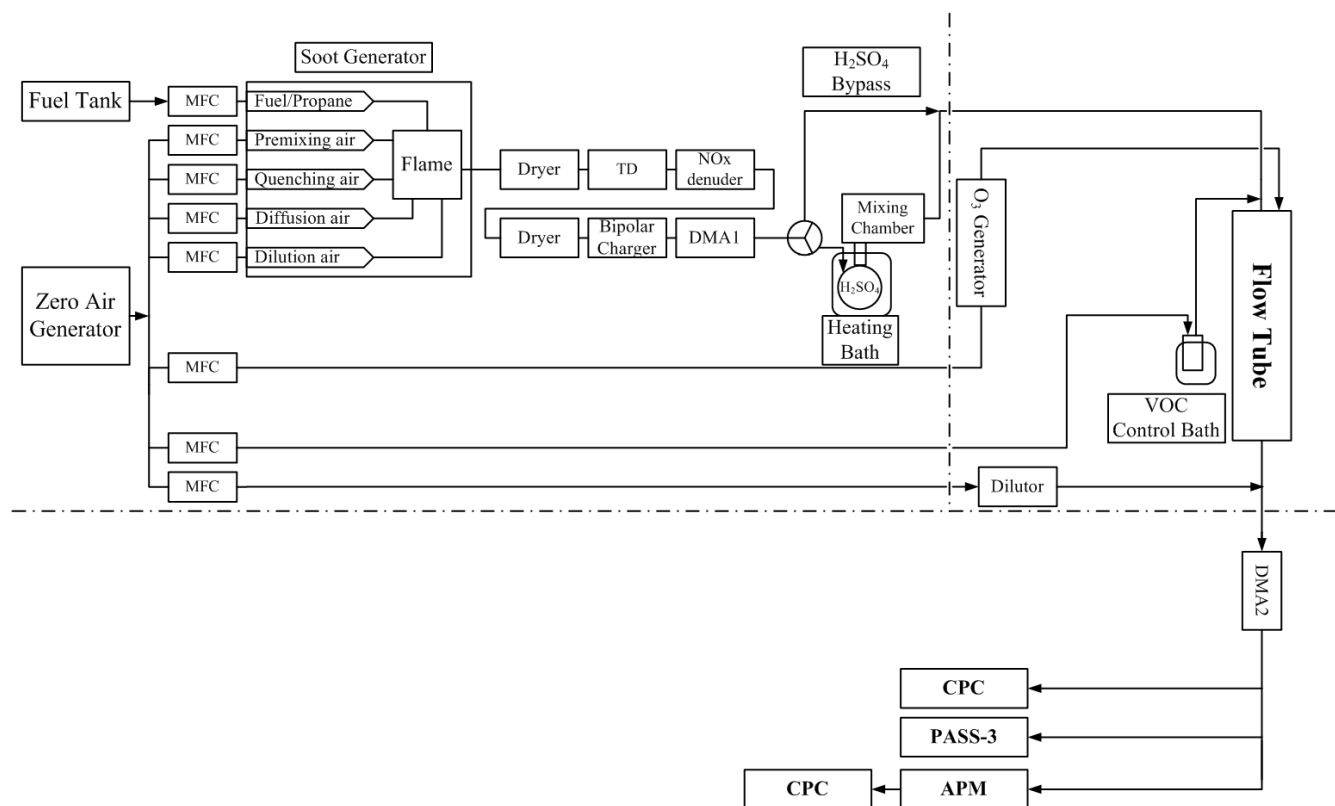
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Table 2. Quantification of volume of condensed material utilized for filling and growth of the mobility diameter when coated with [L-amount-oflarge](#) sulfuric acid and [L-amount-oflarge](#) SOA. Results of other cases are shown in Table S2 of the supplement.

Soot core D_p (nm)	Soot Core F_{vs} (%)	Δr_{me} of coated particle (nm)	Δr_{me} of filling (nm)	Δr_{me} for growth (nm)	Volume of total coating material (×10 ⁵ nm ³)	Volume of material used for filling (×10 ⁵ nm ³)	Volume of material used for growth (×10 ⁵ nm ³)	Volume of soot core void space (×10 ⁵ nm ³)	Fract ion of void space filled (%)	% of material went to filling	% of material went to growth	Fract ion of internal voids (%)	Fract ion of open voids (%)
75	58	52.1	9.3	42.8	21.00	1.30	19.70	1.33	97	6	94	90	10
100	63	36.9	7.3	29.6	13.90	1.40	12.50	3.20	44	10	90	91	9
150	72	35.2	12.4	22.8	19.29	4.54	14.75	11.78	38	24	76	91	9
200	78	30.5	20.5	10.0	20.92	12.13	8.79	29.50	41	58	42	83	17

Table 3. Literature values reported for fraction of void space, internal voids, open voids, and void space filled at $\Delta r_{me} = 20$ nm compared with the values obtained in this study.

	Fraction of void space, F_{vs} (%)	Fraction of internal voids, F_i (%)	Fraction of open voids, F_o (%)	Fraction of void space filled, $F_{vs,f}$ (%) at $\Delta r_{me} = 20$ nm
Qiu et al. (2012)	76	16	84	126
Guo et al. (2016)	77	5	95	169
This study	63	91	9	18



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Figure 1. Schematic of the experimental setup.

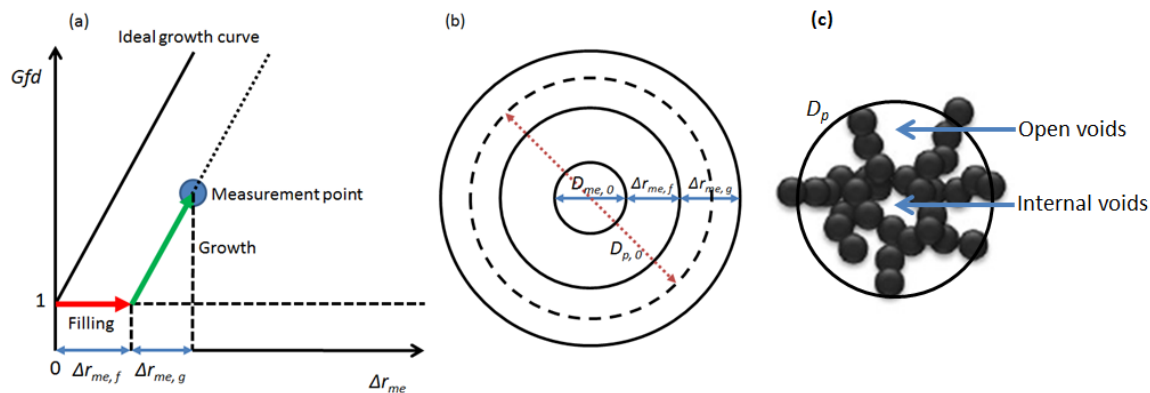
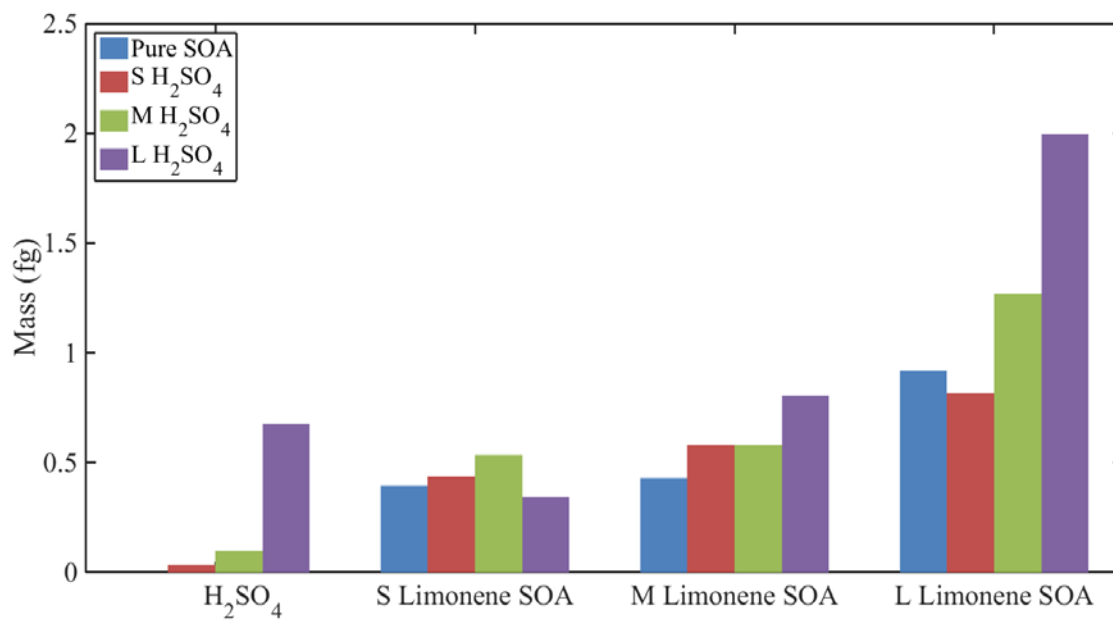
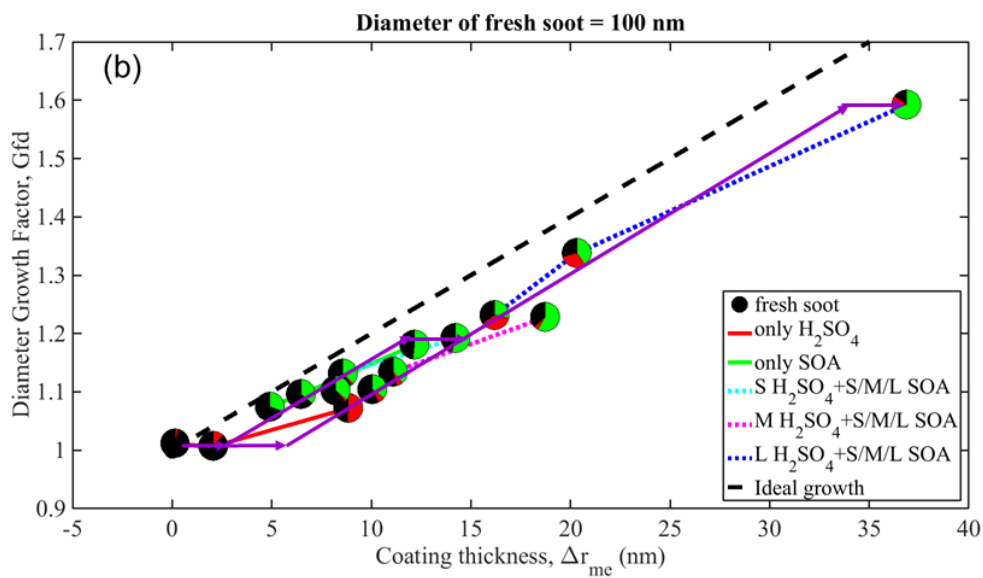
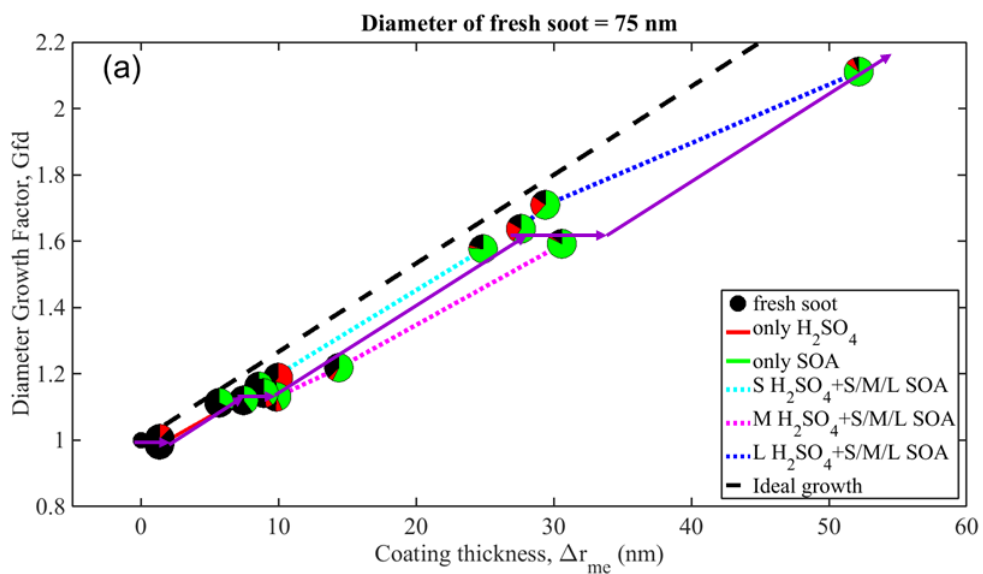


Figure 2. Illustration of the framework for quantifying the morphological transformation and structure of soot aggregate.



5 Figure 3. Mass associated with different levels of sulfuric acid and SOA coatings for the 200 nm soot core.



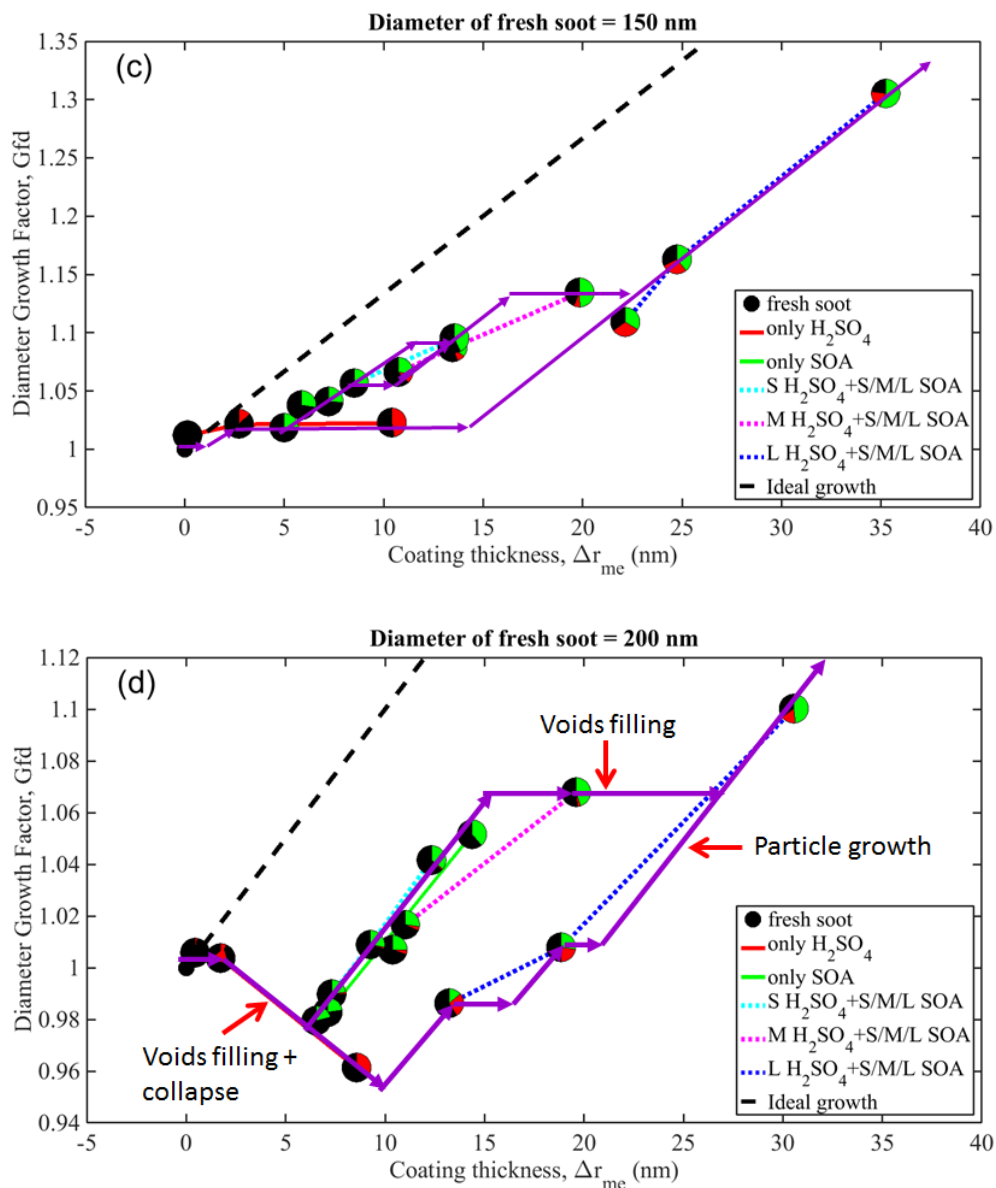


Figure 4. Mobility diameter growth factor (Gfd) with initial fresh soot mobility diameter of 75, 100, 150, and 200 nm as a function of the mass equivalent coating thickness (Δr_{me}). The black, red, and green colors in each pie chart represent the mass fraction of black carbon, sulfuric acid, and organics calculated from Eq. (4)–(6), respectively. Purple lines parallel to the ideal sphere growth line (dashed black) represent growth of the particle diameter; purple lines parallel to the x-axis represent filling of voids; purple lines with negative slope indicates a combination of voids filling and collapse of the soot particle.

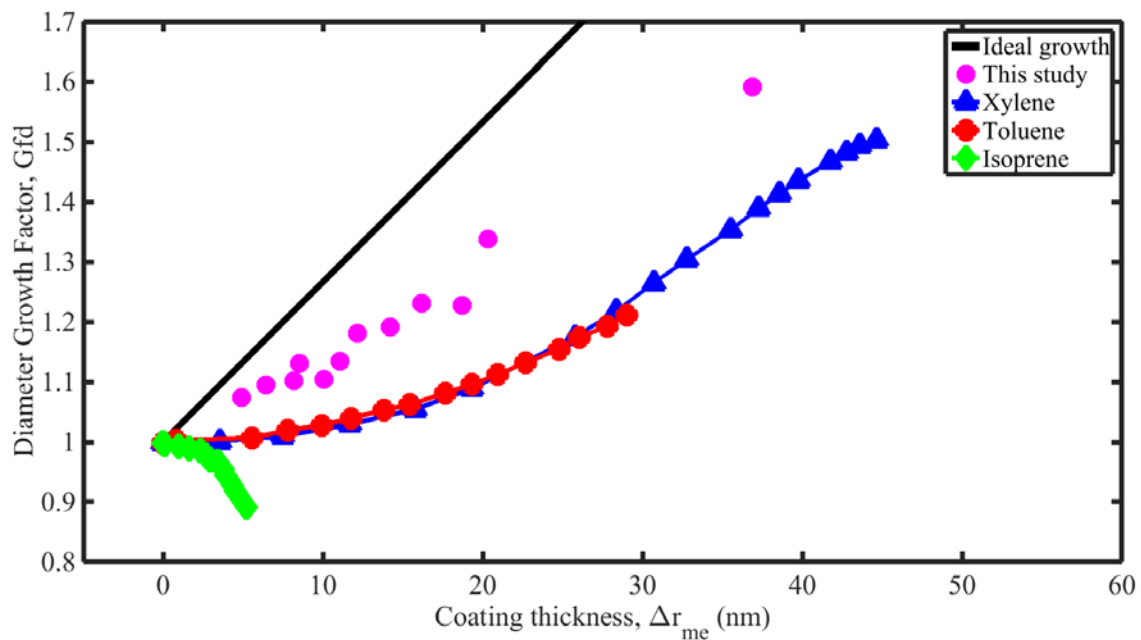
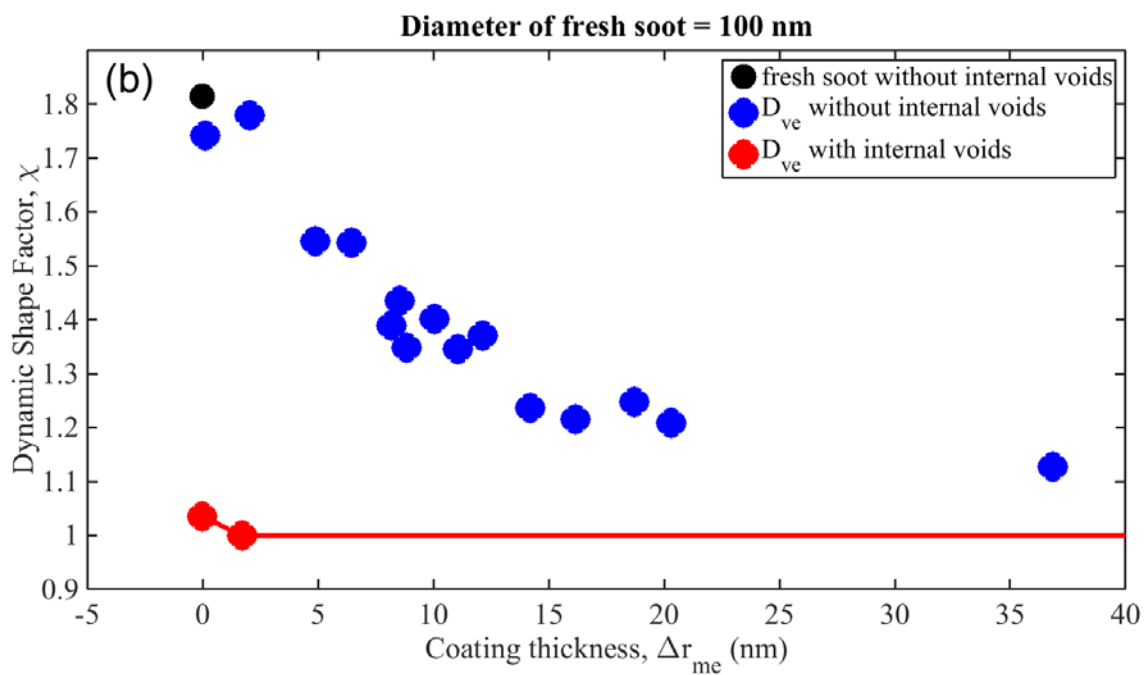
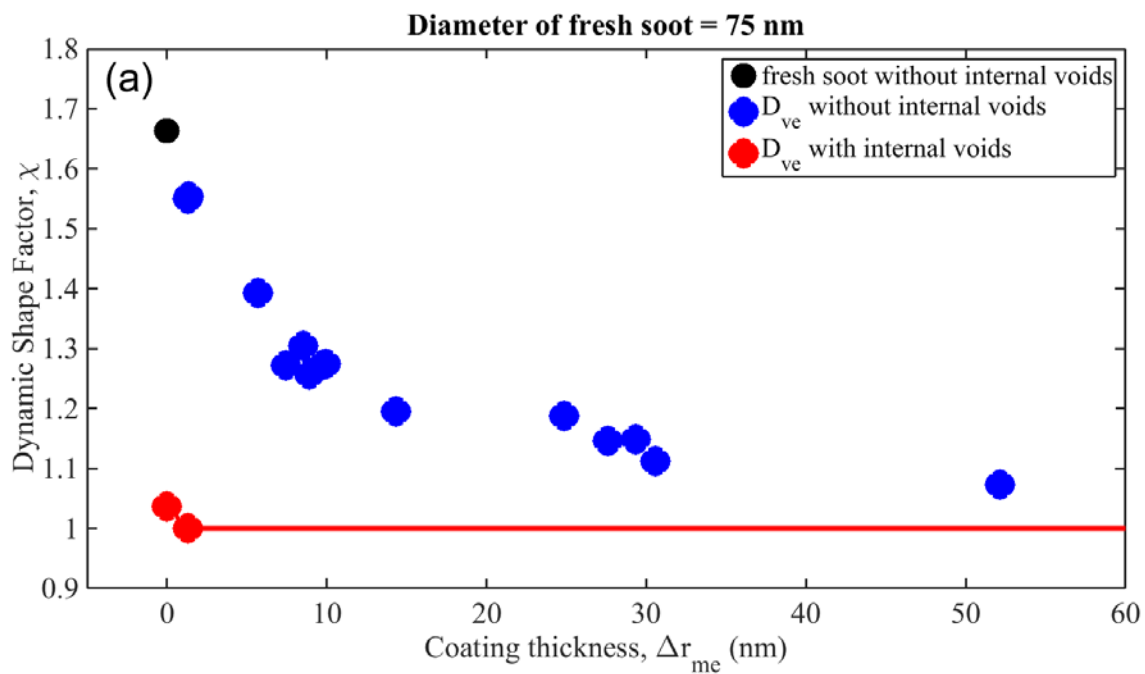


Figure 5. Mobility diameter growth factor (Gfd) with initial fresh soot mobility diameter of 100 nm as a function of the mass equivalent coating thickness (Δr_{me}) reported in the literature and obtained in this study.



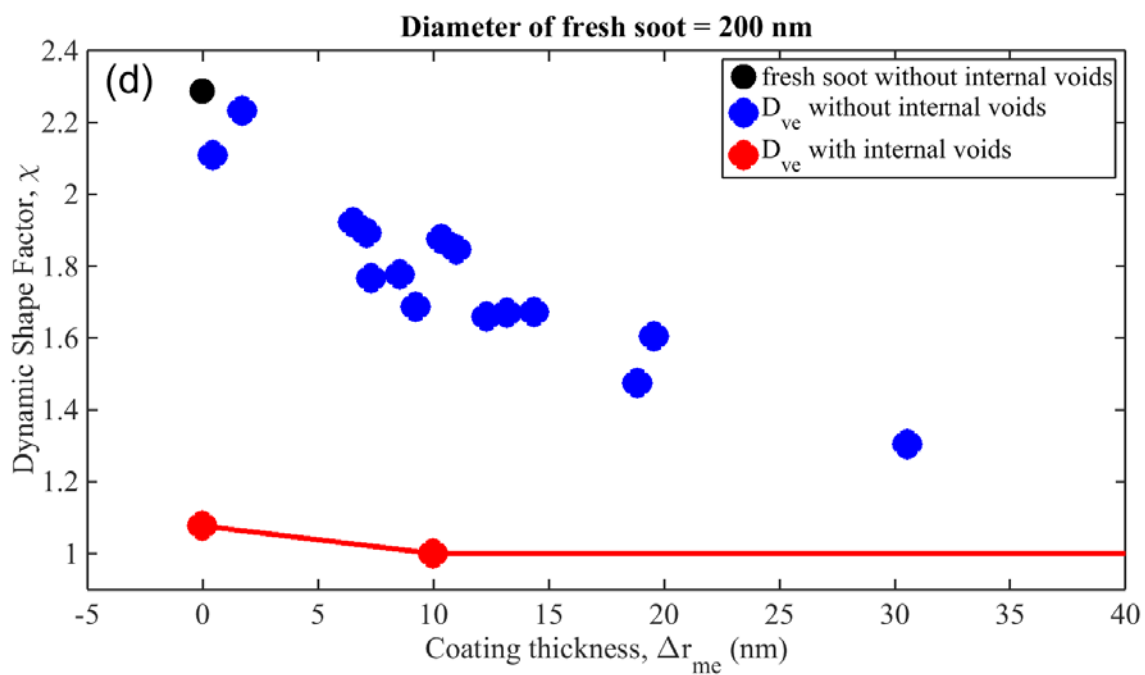
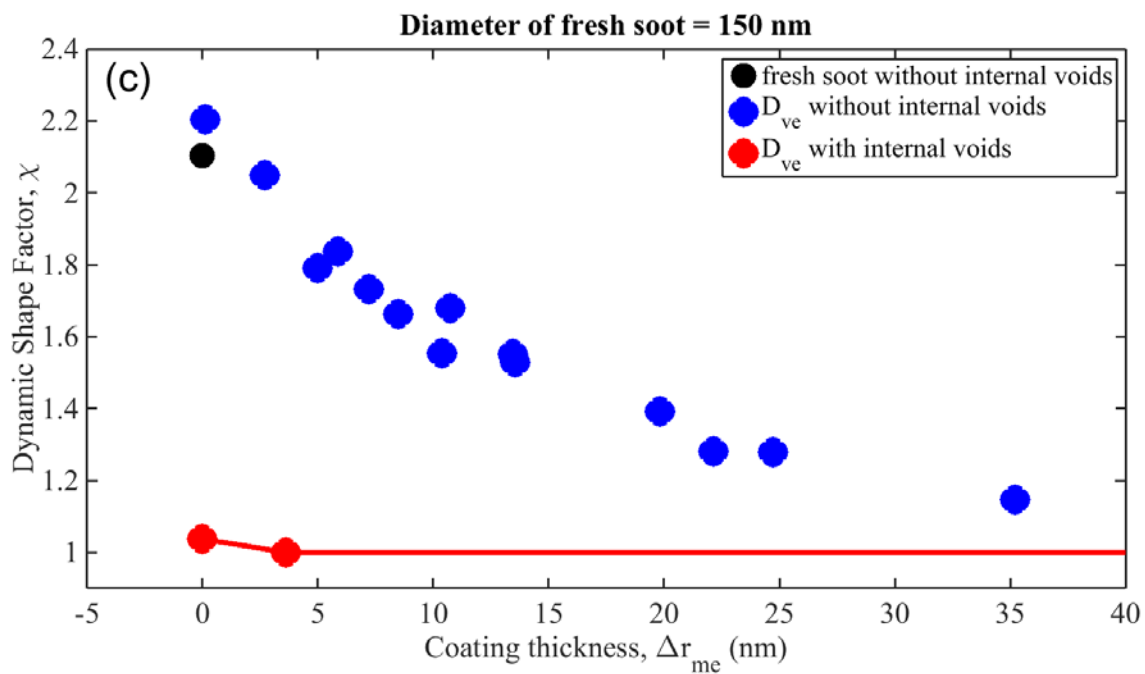
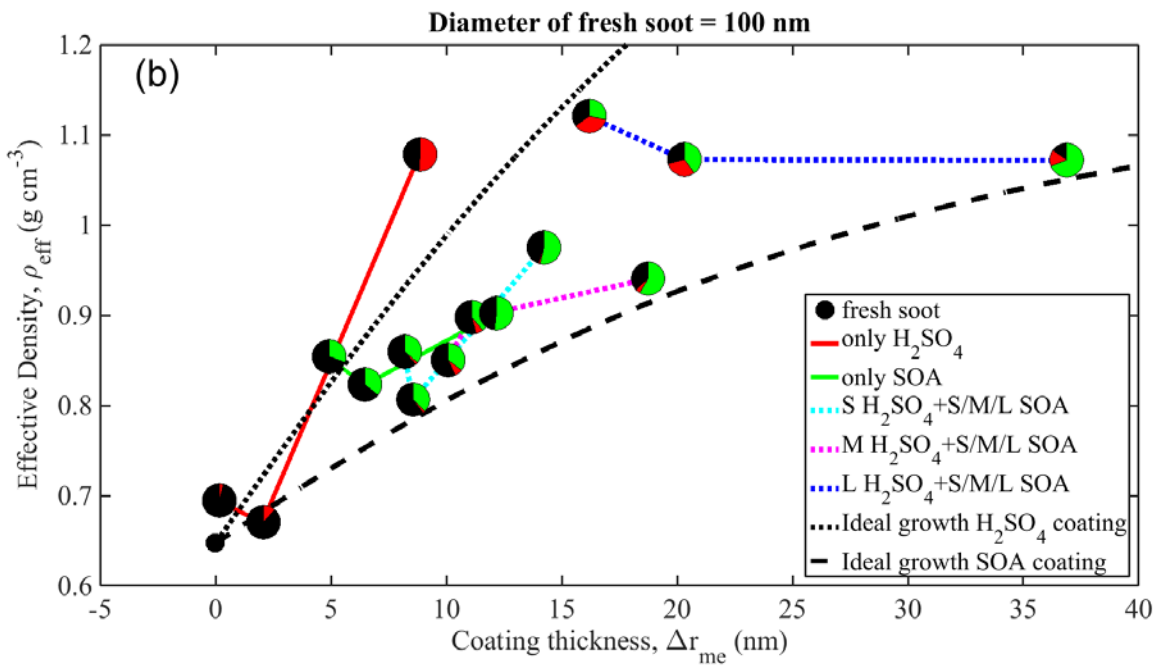
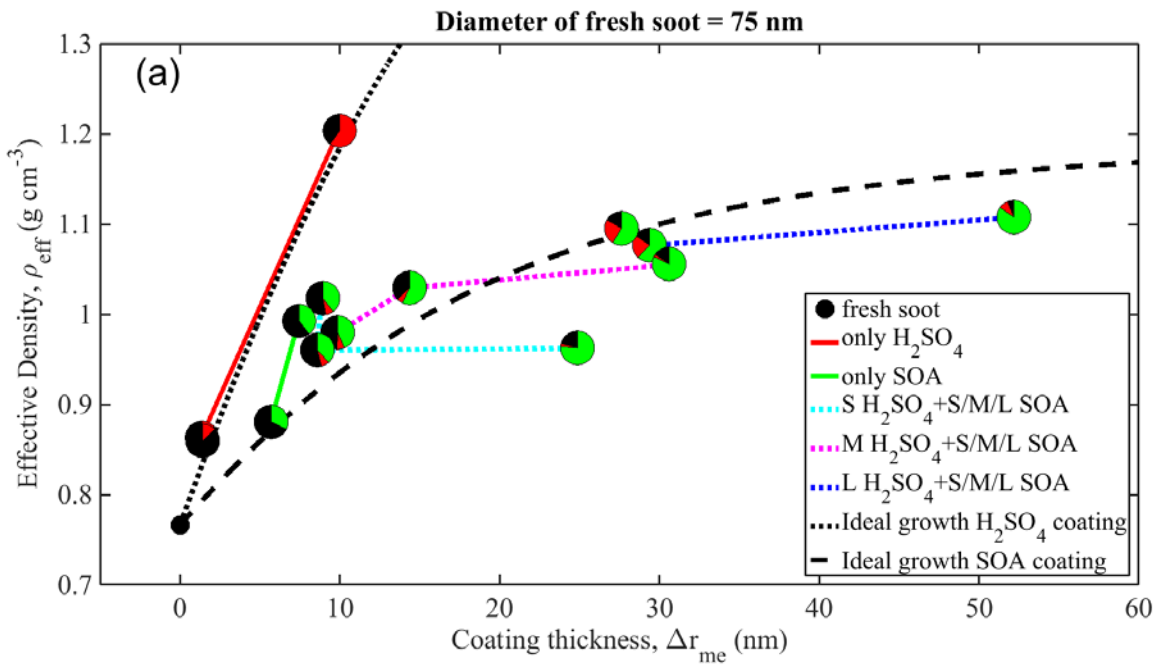


Figure 6. Dynamic shape factor (χ) of fresh and processed soot particles as a function of the mass equivalent coating thickness (Δr_{me}).



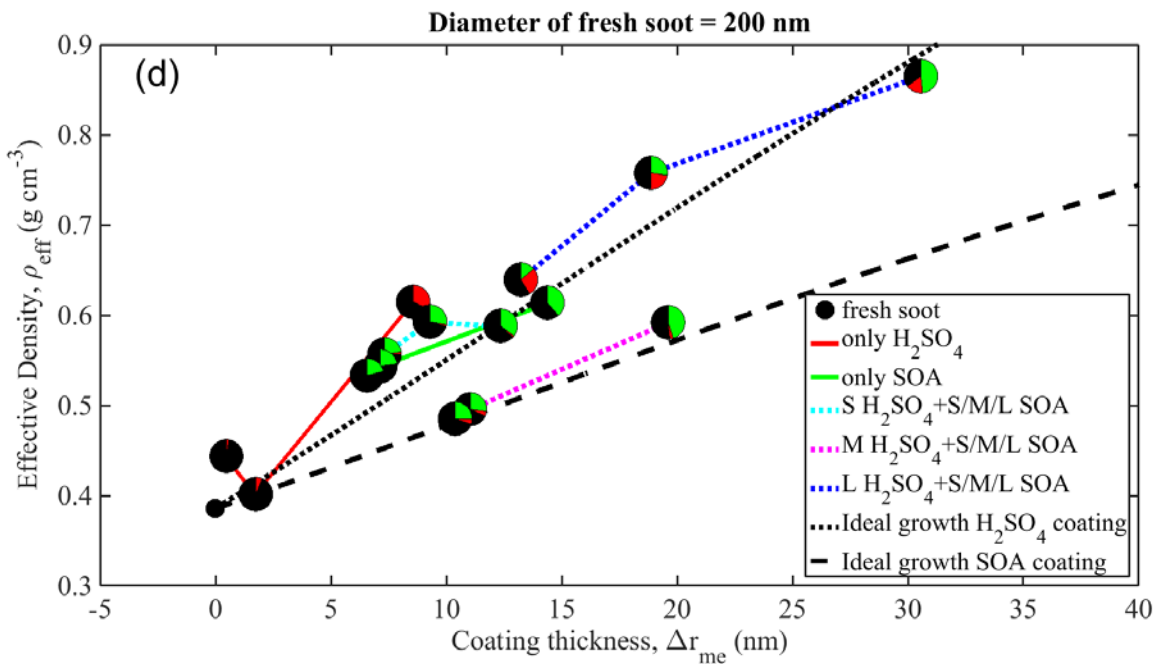
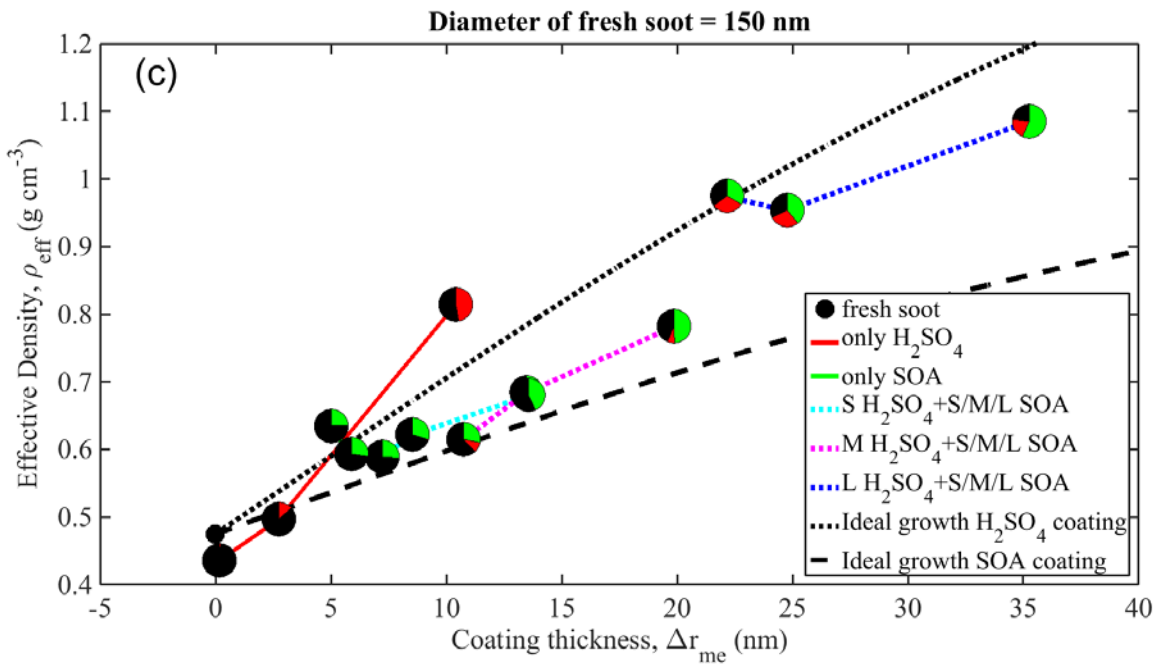


Figure 7. Effective density (ρ_{eff}) of fresh and processed soot particles as a function of the mass equivalent coating thickness (Δr_{me}).