Dear Editor,

We would like to thank you for the time you spent on the manuscript and finding the reviewers. The answers to the review comments were submitted as supplement files on 16 January, 2015, and we have modified the manuscript according to the responses to the reviewer comments (see the responses below, also posted online in the Interactive Discussion). We have also updated the reference list, and corrected a few small typos in the manuscript. We hope that you can consider our manuscript for publication in Atmos. Chem. Phys. and are looking forward to any comments you might have.

Best regards,

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Reviewer #1

We thank Reviewer #1 for his/her positive, constructive and detailed comments, which we will account for in the revised manuscript. In particular, we would like to thank the reviewer for requesting a more detailed treatment of the particle shape and its importance for the CCN activation, as we feel that accounting for these comments has improved the manuscript considerably. Our point-by-point responses to the issues raised by the reviewer are below.

Scientific questions:

My only major general comment concerns the agglomeration part of the study. I believe 2 important things are missing:

1) a discussion of why it is important to consider particle shape in the context of the theoretical frameworks that are discussed. Specifically, what are the physical reasons for using the surface equivalent diameter rather than mobility diameter in each term in Eq. 13?

Particle shape can affect the physical dimensions of the particle in terms of the surface available for water vapour to adsorb onto, as well as for the effective curvature determining the Kelvin effect (see e.g. Kumar et al., 2011a). This is particularly relevant for the adsorption term in Eq. 13 describing the attachment of water molecules on the insoluble silica surface – where the available surface is the key parameter to be known for predicting the adsorption rates correctly. For the solution term, on the other hand, the total amount of soluble material (related to the particle density) is the relevant property to know. In the case of highly non-spherical or porous particles the conversion between the electrical mobility (the quantity measured with the SMSPS system) and the available surface area or particle volume and density is not straight-forward. In our case, we used measurements of particle mass for the pure silica agglomerates to complement the information about the mobility of these particles. The results suggested that the particles were somewhat in agglomerated shape (fractal dimensions of about 2.55 as compared with 3 for spherical particles) and porous. We have added a brief discussion on the impacts of particle shape on CCN activation to the revised manuscript.

In the present paper we used the surface equivalent diameter to account specifically for the larger surface area available for the adsorption on the insoluble silica fraction. This has some implications for the fitted FHH parameters (see our responses to the next comment and Figs. R1-R4). However, as mentioned above, the volume (or mass) equivalent diameter is probably more relevant metric for terms describing the solute effects in Eq. 13. In the case where the surface and the volume equivalent diameters are very different from each other (e.g. highly branched chain-like agglomerates), the two diameters differ from each other (surface equivalent diameter is larger than the volume equivalent diameter), and the former is more appropriate for describing the adsorption phenomena and the latter the solute effect. For close-to-spherical compact agglomerates the surface and volume equivalent diameters are, on the other hand, equal to each other and the mobility diameter (but larger than the mass equivalent diameter).

Based on our additional analysis of the particle shape (see the response to the next comment and Figs. R1-R4) we conclude that our particles are closer to porous but compact agglomerates than chain-like structures – in which case the surface and volume equivalent diameters are close to each other and the mobility diameter. In the revised manuscript all the calculations applying Eq. 13 have now been made assuming compact agglomerates with surface equivalent diameter being roughly equivalent to the volume equivalent and mobility diameters. This does

63 *not change any of the conclusions of the manuscript but changes some of the absolute numbers*
64 *to come extent, as illustrated in Figs. R1-R4 below.*

65 2) a study of the sensitivity of predicted critical supersaturations to particle shape. Given the
66   sensitivity of predicted critical supersaturations to the FHH adsorption parameters and
67   soluble volume fraction, and the fact that both of these sets of parameters can be difficult to
68   know for ambient particles, is it even necessary to account for particle shape?

69 *Thank you for raising this issue, which prompted us to do a more systematic analysis of the*
70 *influence of the assumed particle shape/porosity on our results. The sensitivity of the results to*
71 *the particle shape and porosity assumption are illustrated for pure silica and the mixed*
72 *particles in Figs. R1-R4 below. In these figures we have tested two limiting assumptions about*
73 *the particle shape, using the information on the mobility diameter d_b (available from the SMPS*
74 *for both the pure silica and the mixed particles) and the particle mass and mass equivalent*
75 *diameter d_{me} (available from the APM measurements for pure silica). With this amount of*
76 *information at hand (i.e. no direct measurement of the particle density), the two limiting*
77 *assumptions for the pure silica are:*

78   1) *Assuming the silica particles are compact agglomerates having nearly spherical shape*
79   *but internal voids. In this case the mobility (d_b) and volume equivalent diameters (d_{ve})*
80   *are approximately the same and also equal to surface equivalent diameter (d_{se}), but*
81   *larger than the mass equivalent diameter (d_{me}) i.e. $d_b = d_{ve} = d_{se} > d_{me}$. The particle*
82   *density is in this case lower than the pure silica material density (DeCarlo et al., 2004),*
83   *but equal to the effective density.*

84   2) *Considering the silica particles as chain-like agglomerates with no internal voids, for*
85   *which mass and volume equivalent diameters are equal (DeCarlo et al., 2004), but*
86   *smaller than surface equivalent and mobility diameters, i.e. $d_{ve} = d_{me} < d_{se}$ and d_b. In*
87   *this case the particle density would be the same as the pure silica material density but*
88   *higher than the effective density.*

89 *The predicted critical supersaturations vs. mobility diameters resulting from analysing the*
90 *silica data with these two assumptions are presented in Fig. R1, using the literature values for*
91 *the FHH adsorption parameters A_{FHH} and B_{FHH} (Keskinen et al., 2011; Kumar et al., 2011a),*
92 *or fitting them to our data separately for each assumption – using the surface equivalent*
93 *diameter d_{se} as the dry diameter in Eq. 12. It can be seen that while the assumption on the shape*
94 *does not have a drastic effect on the results, the "compact agglomerates" assumption yields*
95 *higher critical supersaturations for given A_{FHH} and B_{FHH} values as compared with the "chain-*
96 *like agglomerates" assumption. For the case of fitted A_{FHH} and B_{FHH}, on the other hand, the*
97 *assumed shape does not influence the value determined for A_{FHH}, while the B_{FHH} value is*
98 *affected rather significantly. We have discussed this sensitivity of the results to the assumption*
99 *of the silica particle shape in the revised manuscript.*

100 *The fractal dimension D_f determined from the data provides further insight on the sphericity of*
101 *the silica particles (DeCarlo et al., 2004; Boldridge, 2010; Keskinen et al., 2011), for perfect*
102 *spheres $D_f = 3$ and for line-like structures $D_f = 1$. The D_f values determined from our data were*
103 *of the order of 2.54-2.55, thus suggesting closer to spherical rather than rod- or chain-like*
104 *structures. We therefore expect the silica particles to be better represented by the "compact*
105 *agglomerates" assumption above, and have thus used this assumption for interpreting the data*

106 *throughout the revised manuscript (i.e. just present the predictions corresponding to the solid*
107 *lines in the revised manuscript).*
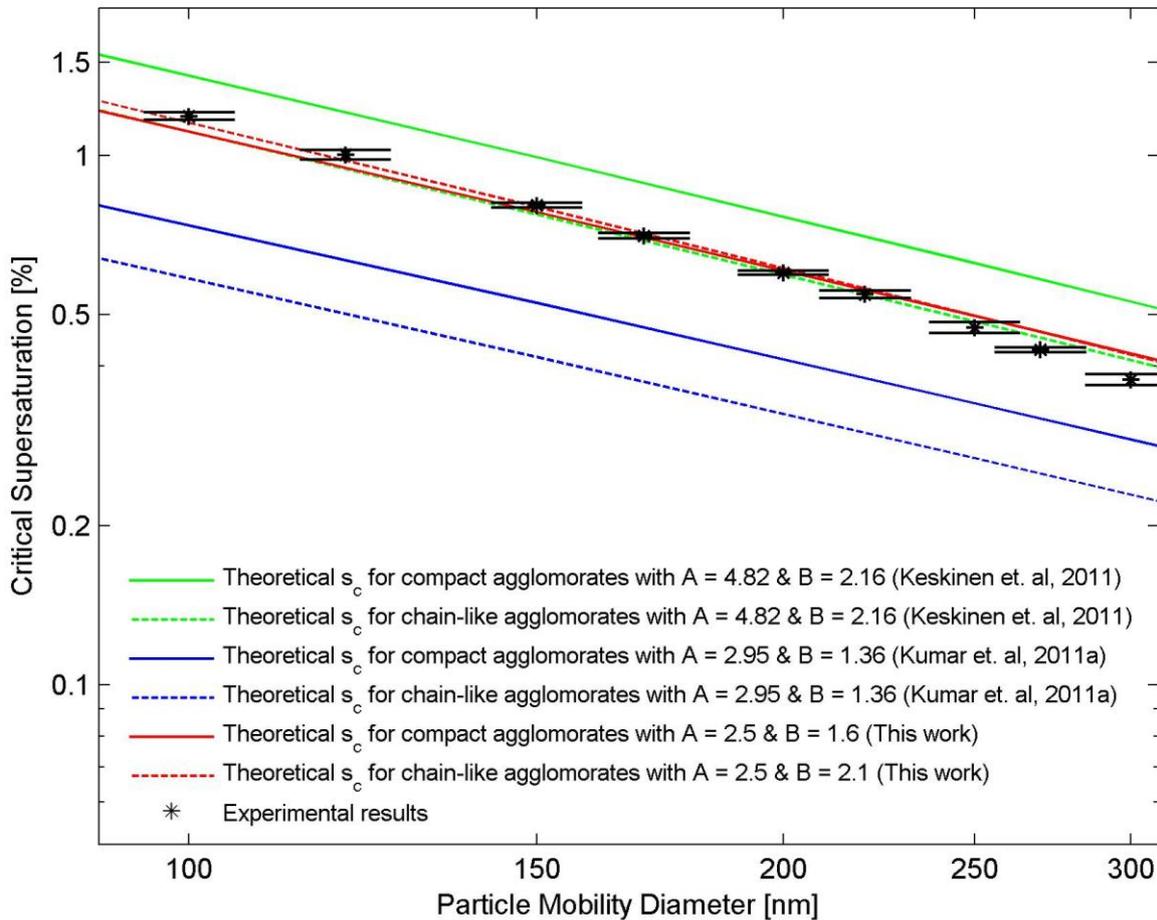
Fig. R1: Critical supersaturations against the critical mobility diameter of pure silica particles with
different FHH adsorption isotherms and assuming either compact but porous agglomerates (solid lines)
or chain-like agglomerates (dashed lines).

112 *As mentioned above, the mass analysis results were only available for the pure silica particles.*
113 *When analysing the CCN activation data for the mixed particles, we assumed that the effective*
114 *density of the silica in the mixed particles was similar to the effective density of the pure silica*
115 *particles. The physical meaning of this assumption in the "compact agglomerates" assumption*
116 *would be that the silica present in the mixed particles would contain the same volume of voids*
117 *per unit silica mass as the pure particles Furthermore, when calculating the critical*
118 *supersaturations using Eq. 13 the adsorption term was calculated using the surface equivalent*
119 *diameter d_{se} as d_{dry} and the solubility term using the volume equivalent diameter d_{ve} as d_{dry}. The*
120 *sensitivity of the critical supersaturation predictions and the corresponding distribution of the*
121 *soluble material calculated this way are presented in Figs. R2-R4. For the mixtures with*
122 *ammonium sulphate (Fig. R2) the assumption about the particle shape does not affect the*
123 *results significantly. For the mixtures with sucrose, a larger sensitivity is observed – the "chain-*
124 *like agglomerates" assumption predicting considerably higher critical supersaturations than*
125 *the "compact agglomerates" assumption for a given constant soluble fraction (Figs. R3a-b).*
126 *In accordance with this, the size-dependent fitted soluble fractions (Figs. R3c-e) assuming*

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127 *compact agglomerates are lower than the corresponding values for the chain-like assumption.*
128 *In fact, it is notable that the soluble fractions fitted for the chain-like assumption are*
129 *consistently higher than the soluble fraction in the atomized solution – which is probably not*
130 *realistic. This further suggests that the "compact agglomerate" assumption is probably more*
131 *reasonable in the case of the mixed particles containing silica and sucrose. The corresponding*
132 *results for the mixed silica + BSA particles are shown in Fig. R4. First, it should be noted that*
133 *the different mixture compositions lie relatively close to each other in terms of their critical*
134 *supersaturations – making it difficult to constrain the soluble contents of these particles.*
135 *However, it seems clear that at the small particle sizes (< 150 nm) the particle population is*
136 *dominated by pure BSA particles. At sizes between 150 and 250 nm, on the other hand,*
137 *extremely low BSA-content is required to reproduce the observed critical supersaturations.*
138 *This is of course also visible in Fig. 8c of the present paper, where the mixtures with low BSA-*
139 *content seem to activate at even higher supersaturations than pure silica. We do not know the*
140 *exact reason for this, but the effect of BSA on silica particle structure (e.g. density etc.) could*
141 *be speculated upon.*

142 *Given these overall results on the sensitivity to the shape assumption, we have applied the*
143 *"compact agglomerate" assumption (i.e. $d_b = d_{ve} = d_{se}$) in all the theoretical calculations (in*
144 *particular Eqs. 12-13) and the corresponding figures of the revised manuscript.*
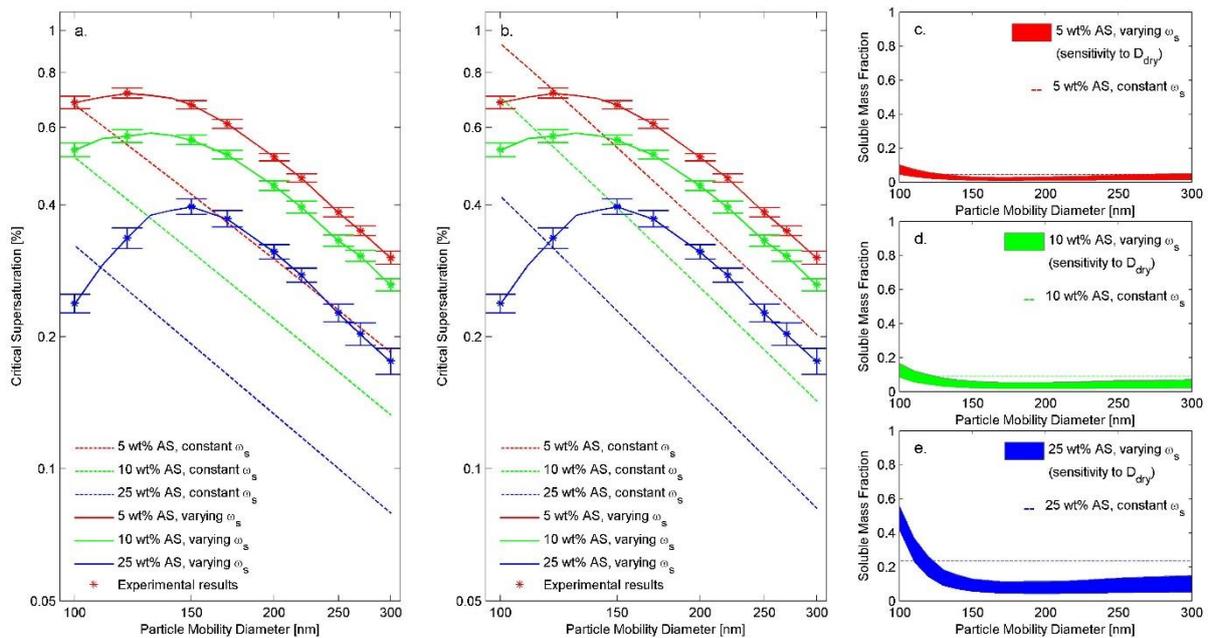
146 *Fig. R2: Experimental and theoretical critical supersaturations for mixed silica + $(NH_4)_2SO_4$ (AS)*
147 *particles vs. particle mobility diameters using different assumptions of particle shape and porosity.*
148 *a) Critical supersaturations calculated assuming "compact agglomerates" for constant and varying ω_s.*
149 *b) Critical supersaturations calculated assuming "chain-like agglomerates" for constant and varying*
150 *ω_s. c-e) The sensitivity of the distribution of soluble material to these two assumptions. The upper limit*
151 *corresponds to the "chain-like agglomerates" assumption and the lower limit to the "compact*
152 *agglomerates" assumption.*

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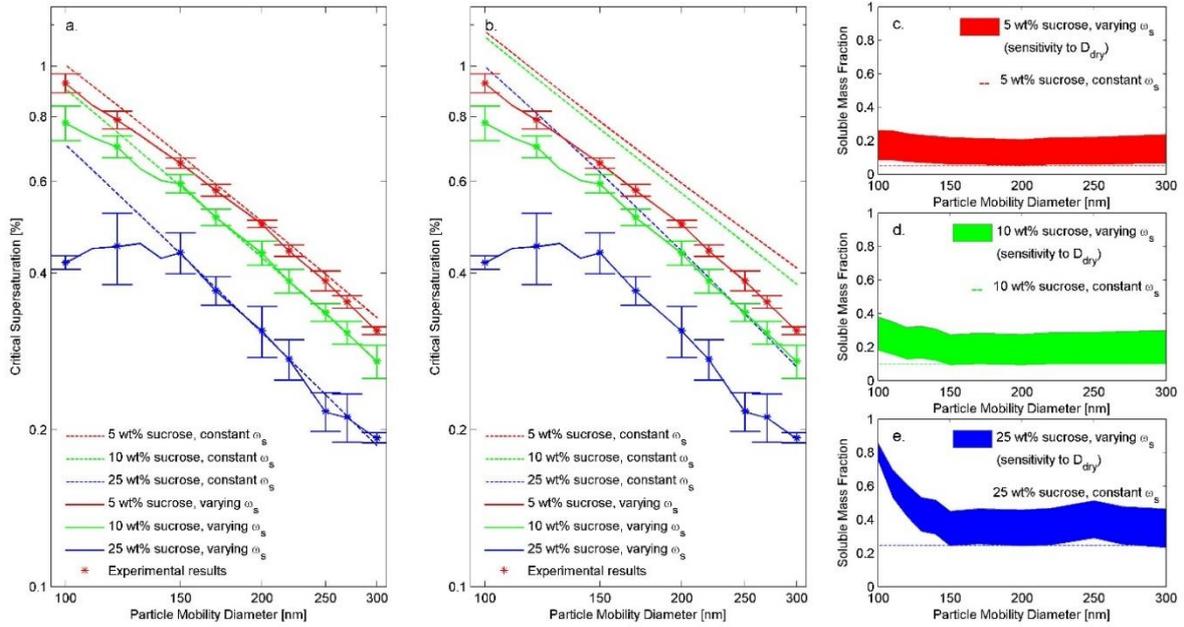
Fig. R3: Experimental and theoretical critical supersaturations for mixed silica + sucrose particles vs. particle mobility diameters using different assumptions of particle shape and porosity. a) Critical supersaturations calculated assuming "compact agglomerates" for constant and varying ω_S. b) Critical supersaturations calculated assuming "chain-like agglomerates" for constant and varying ω_S. c-e) The sensitivity of the distribution of soluble material to these two assumptions. The upper limit corresponds to the "chain-like agglomerates" assumption and the lower limit to the "compact agglomerates" assumption.

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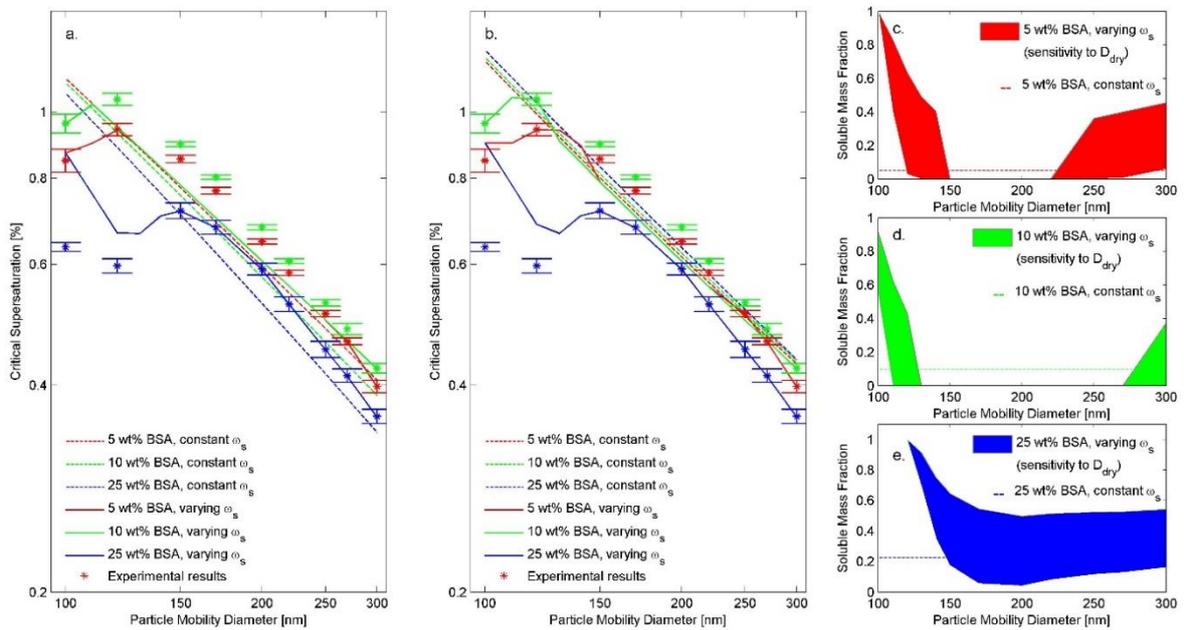
Fig. R4: Experimental and theoretical critical supersaturations for mixed silica + BSA particles vs. particle mobility diameters using different assumptions of particle shape and porosity. a) Critical supersaturations calculated assuming "compact agglomerates" for constant and varying ω_S. b) Critical supersaturations calculated assuming "chain-like agglomerates" for constant and varying ω_S. c-e) The sensitivity of the distribution of soluble material to these two assumptions. The upper limit corresponds to the "chain-like agglomerates" assumption and the lower limit to the "compact agglomerates" assumption.

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Specific comments

P 23174, L18 - It seems the mass measurements were only performed for pure silica particles. What surface equivalent diameters were used for the mixed particles?

The reviewer is correct – the mass measurements were only conducted for pure silica. In the present manuscript the surface equivalent diameters used were in fact calculated using the effective density of silica determined from the mass measurements (and be equivalent to the pure silica particle density, corresponding to the "chain-like agglomerate" assumption) and the material density of the soluble species. However, as clarified above, in the revised manuscript we have rather used the silica particle density determined using the "compact agglomerate" assumption and assuming that $d_b = d_{ve} = d_{se}$.

P 23174, L 24 - Were the contributions of the smaller soluble particle mode subtracted from both the CCN and CN measurements? How were the contributions of the smaller completely soluble particles to CCN concentrations determined? From theory?

First, the contribution of pure soluble particles to the total number of CN for each size were estimated by fitting two log-normal modes to the size distributions such as those shown in Fig. 2. These were then subtracted from the CN data for each size to yield an estimate of the total numbers of mixed CN. Second, using the CCN/CN ratios of the pure soluble particles (shown for 120 nm in Fig. 4) we could estimate the number of CCN originating from pure CN at each mobility diameter and supersaturation. Subtracting this from the total number of CCN, we could yield an estimate for the CCN/CN ratio for the mixed particles, shown in Fig. 8. We have clarified this procedure in the revised manuscript.

P 23175, L 25 - Confusing statement. The AFHH coefficient derived in this work is similar to that reported by Kumar (2011a) but the BFHH coefficients are quite different, which I guess is why the results agree better with the Keskinen (2011) curve than Kumar (20011a) curve in Fig. 6?

Given the results shown in Fig. R1, the "compact agglomerate" assumption actually makes the results for fitted FHH-parameters relatively close to those by Kumar et al. (2011a). We have revised this statement accordingly.

P 23175, L 25 "although the AFHH and BFHH values are close to those reported by Kumar et al. (2011a)" → "B_{FHH} value in this study is closer to that reported by Keskinen et al. (2011)"

Given the revised treatment of the pure silica data, both fitted values are now actually closer to those reported by Kumar et al. (2011a). We have modified the revised manuscript accordingly.

P 23175, L 26 – It's concluded that these data are not sufficient to uniquely constrain the FHH adsorption parameters. What would be sufficient data? Given the complexity of atmospheric aerosols is it reasonable to expect useful FHH adsorption parameters could be obtained for modelling more complex systems?

This is an interesting question, which we do not have a definite answer for. Based on our results it can be seen that in particular parameter A_{FHH}, describing the interactions of the first monolayer and the adsorbate surface, seems to be difficult to constrain based on the CCN activation data (see Fig. 6 in the paper). This is perhaps not surprising as at the point of activation the rapid condensation of water might relatively soon destroy the information of the

very first steps of the adsorption / monolayer formation. For the parameter B_{FHH}, on the other hand, the fits seem to reproduce relatively robust values. CCN activation measurements are probably not the best approach for yielding accurate data of the physical phenomena behind the adsorption parameters – as a lot of information has already been lost at the point where the CCN are activated and detected – but should be rather regarded as a valuable source of information on the processes limiting atmospheric cloud droplet formation. We have added a brief discussion on this to the revised manuscript.

P 23176, L6 - How pure? Need to be more specific since it is not mentioned in the experimental methods section.

De-ionized water with the resistivity > 10 MΩ-cm and TOC concentration $< 5ppb$ was used in our experiments. We have added this information to the revised manuscript.

P 23177, L14 - The structure idea could be tested by exploring the sensitivity of critical supersaturation to particle shape as mentioned above. E.g. Is the range of theoretical predictions of critical supersaturation for realistic shape factors comparable to the differences in critical supersaturation observed in Fig. 8c.

This is a good point. As discussed above, the results do seem to support the idea that the BSA particles affects the stability of the silica particles.

P 23197, Fig 9 - (and Figs. 10 and 11) Recommend keeping the same colour code as Figure 8, red – 5

Thank you for pointing this out. The colour codes for particles corresponding to the 5 & 10 % solute fractions have been exchanged in the Figs. 9, 10 & 11 of the revised manuscript.

Technical comments
P 23171, L18 - Typo in the equation for ε_s

Thank you for pointing this out. We have replaced $\varepsilon = 1-\varepsilon$ with $\varepsilon_s = 1-\varepsilon_i$ in the revised manuscript.

P 23177, L24 and 28 - Typos in ω and ε

Thank you for pointing this out. We have replaced $\omega_s s$ with ω_s and $\varepsilon_s s$ with ε_s in the revised manuscript.

Reviewer #2

We thank Reviewer #2 for his/her positive, constructive and detailed comments, which we will account for in the revised manuscript. Our point-by-point responses to the issues raised by the reviewer are below.

Scientific questions:

I have reservations to word "coating" used in this study, simply I do not see clear experimental evidence, to believe that authors are able to coat silica by mixing it with salt, sugar or protein in water, without any special treatment – high temperatures, oxidation or similar. Even though the authors claim they used hydrophilic fumed silica.

We agree that the term "coating" is not an accurate description of our mixed particles. We have modified the revised manuscript accordingly, using the term "mixture" instead of "coating".

Specific comments

Page 6, mid paragraph about CCNc, it would be good to mention what sheath and sample flows of CCNc were used during the experiment.

We have modified the revised manuscript by adding the following text to the the paragraph in question: "Humidified sheath flow (454 cm^3 min^{-1}) surrounds the sample flow (45.4 cm^3 min^{-1}) in the CCN column to hold it in the centre of the column in the region of maximum supersaturation. The ratio of the flows was thus 1 part of sample air to 10 parts of sheath air and the total flowrate was 500 cm^3 min^{-1}. "

Page 7 eq. 3, is not it enough to make reference only to original source? Why to reference to four manuscripts? Similarly through the whole manuscript.

This is a good point. We have modified the revised manuscript accordingly.

Page 13 starting line 361, authors discuss the use of previously reported kappa parameter from literature, listed in Table 1. Why they do not use their own, as showed in Fig.7? Or were the experimentally obtained kappa values exactly the same as reported in literature? Would be beneficial to see activation curves as a function of mobility diameter for pure compounds, since in Fig 8 the activation curves for 150 nm do not reach unity in activation, especially in the case of ammonium sulphate which is used for CCNc calibration.

We used the literature values for κ of ammonium sulphate (AS) and sucrose to demonstrate the good agreement between our results and previous work on pure component activation. The κ values fitted for AS and sucrose using our experimental data would be 0.78 and 0.08. We have added this information to the revised manuscript. Here we should probably also clarify that all the activation curves that were used in further analysis were normalized, using a correction factor derived from the ammonium sulphate experiments, assuming that AS activation probability reaches unity at high supersaturations. Figs. R1-R3 show the unnormalized data on the activation curves as a function of diameter and supersaturation, as requested by the reviewer. We have clarified the normalization procedure in the revised manuscript and add also the normalized curves (which were used in the analysis) to Fig. 8.

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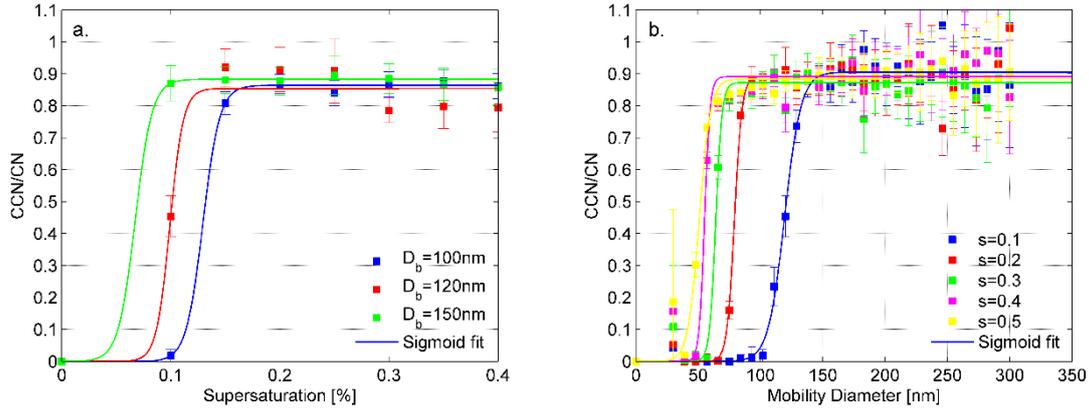
Fig. R1: a) The average activation ratio vs. supersaturation for pure (NH₄)₂SO₄ particles in different mobility diameters. b) The average activation ratio vs. mobility diameter for pure (NH₄)₂SO₄ particles in different supersaturations.

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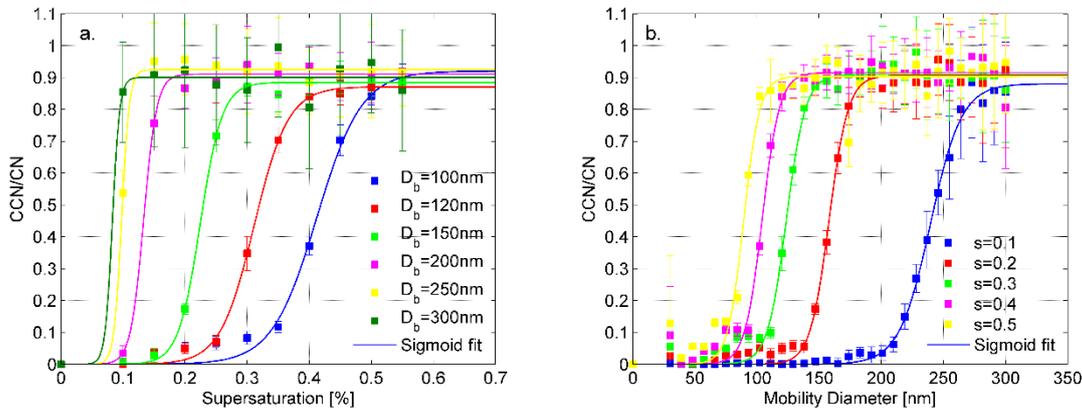
Fig. R2: a) The average activation ratio vs. supersaturation for pure sucrose particles in different mobility diameters. b) The average activation ratio vs. mobility diameter for pure sucrose particles in different supersaturations.

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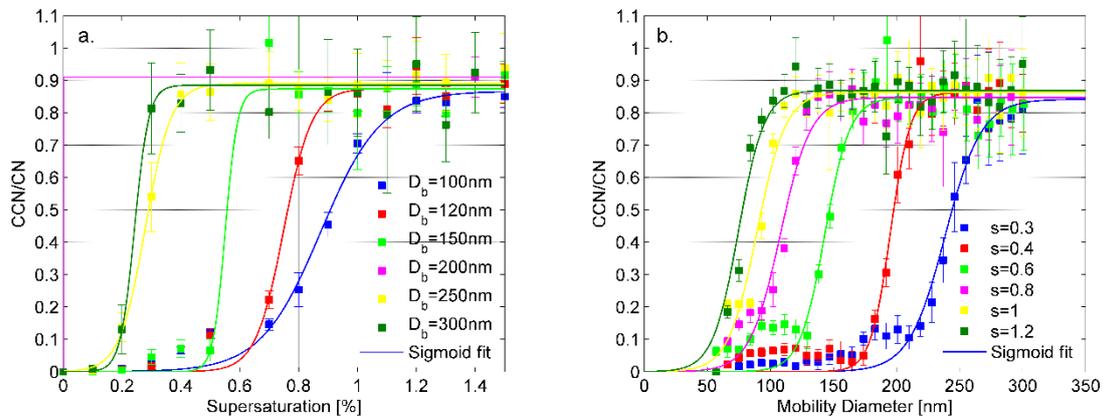
Fig. R3: a) The average activation ratio vs. supersaturation for pure BSA particles in

different mobility diameters. b) The average activation ratio vs. mobility diameter for pure

BSA particles in different supersaturations.

Page 15 line 411, I see this part as very problematic. In Kumar et al (2011b) you can find that they were using several samples of real mineral dust collected in several locations. I have no doubts that their samples undergo certain natural process of aging and use of shell-core model in their case is appropriate. However, this is not the case of this study, making water solution/dispersion of fumed silica and ammonium sulphate (max 25% mass fraction) will not lead to any coating. If authors have different opinion I would like to see any proof of that. For example preparing the dispersion, in the same way as in this work, of aquadac (colloidal graphite) and 70 % mass fraction of AS leads only to about 10% of coated particles, the rest is externally mixed. In the case of BC containing particles you can find out the shell thickness using single particle soot photometer (SP2-DMT, CO, USA), in the case of this study I understand that such a kind of analysis is very difficult. On the other hand the presence of externally mixed particles should be visible from activation spectra (CCN/CN vs Dp) as activated fraction plateaus at a value that is different from unity. I would recommend authors broader discussion with justification for usage of shell-core model or simply omit this part. I am not sure if sucrose and BSA are doing better job in coating than AS.

We fully agree that our mixed particles are not exactly coated, and, as also stated above, we will removed the term "coating" when referring to our mixed particles throughout the text in the revised manuscript. Indeed, there is a wide range of compositions present at a given size range, as also shown in our Figs. 8-11 for all the soluble compounds. However, we also agree that if two distinct aerosol populations (e.g. "mixed" and "pure" particles) we present as a simple external mixture we should see two plateaus in the CCN activation curve – which we don't. Instead, we see a relatively shallow CCN/CN vs. supersaturation curve (see Fig. 8), supporting the hypothesis of a continuous distribution of soluble vs. insoluble volume/mass fractions in the particles – as also indicated by the results shown in Figs. 9-12 in the manuscript. We tried to highlight this in the sentence describing these figures beginning with: "The small contribution of the adsorption term to the theoretical predictions combined with the shallow activation ratio curves (see Fig. 8) suggest that the reason for the apparent discrepancy between the theoretical and the observed critical supersaturations is a non-constant distribution of the soluble material with varying particle size." Also, while the model by Kumar et al. (2011b) was indeed originally introduced for fresh dust coated by a layer of soluble salt after aging, which is not the case for our experiments, it is currently the only readily applicable theoretical formation, and we believe it does give a reasonable estimate on the potential importance of the adsorption as compared with the bulk solubility of the mixed particles. We have clarified this and discuss the limitations of our approach more thoroughly in the revised manuscript.

Page 17 sentence starting on line 498: Similarly as the previous comment, "Our mixed particles : : : representing an aerosol population with various degree of aging in atmosphere." I have hard time to agree with such conclusion. I would encourage the authors to provide any arguments to support use of word "aging". Fig 9-11 shows directly disagreement with shell-core model.

340   *We agree with you. We have removed this sentence and modified the revised manuscript*
341   *accordingly.*

342   Fig. 3 would be nice to see some statistical measure of the fits, e.g. coefficient of determination.

343   *We have added the R^2 values for the fits to Fig. 3 in the revised manuscript (see below).*

344   *In Fig. 3a: $R^2=0.992$*

345   *In Fig. 3b: $R^2=0.978$ & 0.997*

346   *In Fig. 3c: $R^2=0.991$*

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CCN activation of fumed silica aerosols mixed with soluble pollutants

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Abstract:

Particle-water interactions of completely soluble or insoluble particles are fairly well understood but less is known of aerosols consisting of mixtures of soluble and insoluble components. In this study, laboratory measurements were performed to investigate cloud condensation nuclei (CCN) activity of silica particles ~~coated~~ mixed with ammonium sulphate (a salt), sucrose (a sugar) and bovine serum albumin known as BSA (a protein). ~~In addition, t~~The agglomerated structure of the silica particles was investigated ~~by estimating the surface equivalent diameter based on~~using measurements with a Differential Mobility Analyzer (DMA) and an Aerosol Particle Mass Analyzer (APM). Based on these data, the particles were assumed to be compact agglomerates when studying their CCN activation capabilities. ~~By using the surface equivalent diameter the non-sphericity of the particles containing silica was accounted for when estimating CCN activation.~~ Furthermore, ~~characterizing~~ the critical supersaturations of particles consisting of pure and mixed soluble ~~on~~ and insoluble compounds were explored using existing theoretical frameworks. These results showed that the CCN activation of single component particles was in good agreement with Köhler and adsorption theory based models when the agglomerated structure was accounted for. For mixed particles the CCN activation

378   was governed by the soluble components, and the soluble fraction varied considerably with

379   particle size for our wet-generated aerosols. Our results confirm the hypothesis that knowing

380   the soluble fraction is the key parameter needed for describing the CCN activation of mixed

381   aerosols, and highlight the importance of controlled coating techniques for acquiring a detailed

382   understanding of the CCN activation of atmospheric insoluble particles mixed with soluble

383   pollutants.

384

385   *Keywords*: Silica, CCN activation, Mixture aerosols, ~~Soluble coatings~~

1 Introduction

The atmosphere of the Earth is composed of gases and suspended liquid and solid aerosol particles of different size, shape, and chemical composition. Atmospheric aerosols have several important impacts on the environment. First, at high concentrations in urban areas, they are a health hazard to the respiratory system causing millions of premature deaths every year ~~(Jacob, 1999; Mackay and Mensah, 2004; Pope and Dockery, 2006; Pope et al., 2009; Tranfield and Walker, 2012)~~(Mackay and Mensah, 2004; Pope and Dockery, 2006; Pope et al., 2009). Second, they scatter and absorb solar and thermal radiation and thereby directly influence the heat balance of the Earth and thus the climate ~~(Twomy, 1974; McCormick and Ludwig, 1976; Jacob, 1999; Haywood and Boucher, 2000; Ramanathan et al., 2001; Lohmann and Feichter, 2005)~~ (McCormick and Ludwig, 1976; Haywood and Boucher, 2000; Ramanathan et al., 2001). Third, they act as cloud condensation nuclei (CCN) and ice nuclei (IN). Hence, they alter the microphysical properties of clouds and thereby indirectly affect the climate ~~(Twomey, 1974; Twomey et al., 1984; Albrecht, 1989; Jacob, 1999; Haywood and Boucher, 2000; Lohmann and Feichter, 2005; Mcfiggans et al., 2006)~~ (Twomey, 1974; Albrecht, 1989; Lohmann and Feichter, 2005). Fourth, atmospheric surface and condensed-phase chemistry can occur in the aerosol phase ~~(Jacob, 1999)~~(Ravishankara, 1997; Seinfeld and Pandis, 2006).

Aerosol-cloud interactions represent the largest uncertainty in predictions of the future climate (IPCC, 2013)~~(Carslaw et al., 2013; IPCC, 2013; Lee et al., 2013)~~. To reduce this uncertainty we need to improve our understanding of the activation of aerosol particles to cloud droplets. In general, the ability of aerosol particles to act as CCN depends on their composition, size and structure (Kumar et al., 2011a). Besides soluble aerosol particles, insoluble particles like soot, mineral dust, and silica can act as CCN – particularly if they are coated with hygroscopic material (Kumar et al., 2009).

During atmospheric transport and aging, originally insoluble particles may acquire soluble species like $(NH_4)_2SO_4$ (ammonium sulphate) on their surfaces (Levin et al., 1996). In such cases, the threshold supersaturation of cloud droplet activation substantially decreases when water adsorbs onto the slightly soluble particles giving rise to the process of adsorption activation (Saathoff et al., 2003; Hings et al., 2008). Thus, the presence of soluble species on insoluble particle surfaces can enhance water-particle interactions and CCN activity of the particles. Several recent studies have focused on the CCN activation of insoluble and mixed soluble-insoluble particles, leading to the development of new theoretical frameworks for describing the relevant phenomena. The developed theories are often based on multilayer

adsorption models and account for the curvature effects of the particles. One of these theories introduced by Sorjamaa and Laaksonen (2007) combined FHH (Frenkel, Halsey and Hill) adsorption isotherms and traditional Köhler theory to describe the equilibrium growth of insoluble particles. Sorjamaa and Laaksonen (2007) showed that adsorption could help wettable insoluble compounds to activate in the atmosphere. Thereafter, Kumar et al. (2009) developed a cloud droplet formation parameterization where the CCN constitute an external mixture of soluble aerosol, that follows Köhler theory, and insoluble aerosol, that follows FHH adsorption activation theory (FHH-AT). They tested the new parameterization by comparing it to a numerical cloud model and found a good agreement between the parameterization and the model. Later Kumar et al. (2011a) reported laboratory measurements of CCN activity and droplet activation kinetics of aerosols dry generated from clays, calcite, quartz, silica and desert soil samples. They used FHH adsorption activation theory for describing fresh dust CCN activity and found that the adsorption activation theory describes fresh dust CCN activity better than Köhler theory. Afterward, Kumar et al. (2011b) studied particle size distributions, CCN activity, and droplet activation kinetics of wet generated aerosols from mineral particles and introduced a new framework of CCN activation of dust containing a soluble salt fraction, based on a combination of the traditional Köhler and FHH adsorption theories. Henning et al. (2010) on the other hand, studied agglomerated soot particles coated with levoglucosan and ammonium sulphate, and concluded that traditional Köhler theory was sufficient to describe the CCN activation of these mixed particles – as long as the amount of soluble material in the particles was known (see also Stratmann et al., 2010). Despite these pioneering studies, CCN activation measurements of partly insoluble particles containing a soluble fraction are still scarce.

Combustion processes result in emissions of different types of anthropogenic nanoparticles. Flame-made (fumed) silica (SiO_2) particles, mainly produced in flame reactors, are among these kind of particle types (Scheckman et al., 2009). Recently, fumed silica particles have been taken into consideration due to their industrial importance (Scheckman et al., 2009; Keskinen et al., 2011). In this study we use fumed silica particles as an experimental model to investigate the CCN activation of the insoluble and partly soluble particles and the applicability of the current theoretical frameworks developed to describe this phenomenon. Furthermore, since the presented theories generally assume that the insoluble particles are spherical, the agglomerated structure of the silica particles could cause uncertainties in the CCN activation parameterizations. Taking into account the shape characterization of aggregated silica particles may overcome these uncertainties. Different studies have recently focused on parameterizing

452 the structure of aggregated particles, especially silica agglomerates (Fuchs, 1964; DeCarlo et

453 al., 2004; Virtanen et al., 2004; Biskos et al., 2006; Scheckman et al., 2009).

454   The main aims of this study are: 1) measuring the CCN activity of pure and mixed

455 soluble-insoluble particles, 2) analysing and comparing the experimental results with

456 theoretical calculations using the existing frameworks and 3) connecting the mass analysis and

457 shape characterization of agglomerated silica particles to the existing theoretical frameworks to

458 gain a better understanding of the structure effects of these particles. Laboratory measurements

459 on the particle size distribution, mass, morphology and CCN activation of insoluble fumed

460 silica mixed with different amounts of soluble materials ~~were~~ have been conducted.

461 Furthermore, the experimental CCN activity results ~~were~~ are compared to theoretical

462 calculations using the framework introduced by Kumar et al. (2011b), and the distribution of

463 soluble material on wet-generated particle populations ~~is~~ was discussed.

464

2 Experimental setup

466 Pure soluble or insoluble and mixed soluble-insoluble particles were generated and analysed in

467 this study. The investigated mixed particles consisted of fumed silica (Degussa, Aerosil-90) as

468 the insoluble part and three different hygroscopic components as the soluble part. The first

469 hygroscopic component was ammonium sulphate which is a water-soluble inorganic salt with

470 high hygroscopicity (Table 1); the second one was sucrose which is a sugar, i.e. a water-soluble

471 organic; the third one was bovine serum albumin (BSA) which is a large water-soluble protein

472 with molecular dimensions of approximately $4 \times 4 \times 14$ nm (Sugio et al., 1999; Jeyachandran

473 et al., 2010) . The SiO_2 used in the experiments was hydrophilic fumed silica, with a specific

474 surface area of 90 m^2/g and purity of $\geq 99.8\%$ from Evonik Industries. Ammonium sulphate

475 and BSA were purchased from Sigma-Aldrich, and sucrose was purchased from VWR

476 International BVBA. All chemicals had purities higher than 99%.

477   Figure 1 shows a schematic of the experimental setup used in this study. Pure silica and

478 pure soluble particles as well as mixed particles made of silica and soluble species were

479 produced using the atomization-drying method described in Keskinen et al. (2011). Particles

480 were generated by an aerosol generator (Model 3076, TSI Inc., USA) after dissolving materials

481 in de-ionized water (Model Maxima LS., USF Elga Ltd.) with the production resistivity > 10 MΩ-

482 cm and TOC concentration < 5 ppb. The solute content in the water suspension was 0.06 wt%.

483 For mixed particles, the ratios of soluble components to silica were 1:19, 1:9 and 1:3, implying

that the fractions of soluble species were expected to be 5%, 10% and 25% of total particulate mass in the atomized solution. We use the term solution, despite the fact that the insoluble silica particles were suspended in the water (instead of dissolved).

   After the particles had been produced they were fed into a diffusion drier (Fig. 1) consisting of a porous tube surrounded by silica gel (Rotronic AG, model HC2-C04), resulting in a relative humidity (RH) below 5% and they were neutralized using a charge neutralizer. Thereafter particle number size distributions were measured using a Scanning Mobility Particle Sizer (SMPS). The SMPS system was composed of an electrostatic classifier, which included a Differential Mobility Analyzer (DMA) (Model 3071; TSI, Inc.) to bin the particles according to electrical mobility, and an ultrafine Condensation Particle Counter (CPC Model 3025; TSI, Inc.) to count the size-binned particles exiting the DMA.

   Simultaneously, size-resolved CCN activity of the generated particles was measured using a CCN counter (CCNc; Droplet Measurement Technologies Inc.) (Roberts and Nenes, 2005) (Fig.1). Before entering the CCNc, particles were size classified by a DMA, of the same model as the DMA used in the SMPS. The CCNc operates by supersaturating sample air to the point where the CCN become detectable particles. Humidified sheath air (454 cm^3 min^{-1}) surrounds the sample flow (45.4 cm^3 min^{-1}) in the CCN column to hold it in the centre of the column in the region of maximum supersaturation. The ratio of the flows was around 1 part of sample air to 10 parts of sheath air and the total flow rate was 500 cm^3 min^{-1}. The supersaturation in the column can could be varied between 0.1% and 1.5%. The total number concentration of the particles entering the CCNc was measured by a CPC (Model 3772; TSI, Inc.) and the number of activated droplets was counted by an Optical Particle Counter (OPC) over 20 size bins in the diameter range from 0.75 to 10 μm.

   The effect of the silica particle morphology on activation was investigated by measuring the mass of size classified particles by Aerosol Particle Mass Analyzer (APM) (model APM-3600; Kanomax Inc.) (Fig. 1) (McMurry et al., 2002; Park et al., 2003a and 2003b). The APM provides a direct relationship between the applied voltage, rotation speed, and particle mass (Liu et al., 2012). Therefore, by measuring the outlet number concentration of the APM corresponding to different applied voltages of the instrument, it was possible to measure the mass distribution of the size selected particles. For each APM voltage, the downstream number concentration was measured by a CPC (Model 3772; TSI, Inc.) (Fig. 1). From the voltage corresponding to the highest concentration the average particle mass was calculated using the following equation (McMurry et al., 2002; Park et al., 2003b):

$$m = \frac{qV}{r^2\omega^2 ln(r_2/r_1)} \tag{1}$$

where m is the particle mass, ω is the APM angular speed, V is the applied voltage, q is the particle charge, and r_1, r_2 and r are the inner, outer and rotating radius of the instrument, respectively.

3 Theoretical frameworks

3.1 Non-sphericity of particles

Particle shape can affect the physical dimensions of the particle in terms of the surface available for water vapour to adsorb onto, as well as for the effective curvature determining the Kelvin effect (see e.g. Kumar et al., 2011a). In the case of highly non-spherical or porous particles the conversion between the electrical mobility (the quantity measured with the SMPS system) and the available surface area or particle volume and density is not straight-forward. As mentioned above, we used measurements of particle mass for the pure silica agglomerates to complement the information about the mobility of these particles.

Two parameters, the dynamic shape factor (χ) and fractal dimension $()$, have been widely used to characterize non-sphericity of aerosol particles. Dynamic shape factor is defined as the ratio of the drag force on the agglomerated particles to the drag force on the volume equivalent spherical particles (χ', volume-based shape factor) or to the drag force on the (or in some studies mass equivalent) spherical particles (χ, mass-based shape factor) (DeCarlo et al., 2004; Fuchs, 1964; Kelly and McMurry, 1992; Kumar et al., 2011b)(DeCarlo et al., 2004; Kelly and McMurry, 1992). , and The fractal dimension (D_f) is the coordination number in the aggregate and links properties like surface area of a particle to the scale of the measurements (Hinds, 1999; Ibaseta and Biscans, 2010). These parameters are applicable to quantify the morphology of agglomorated particles.

The mass-based shape factor is defined as (Kelly and McMurry, 1992):

$$\chi = \chi = \frac{d_b}{d_{me}} \cdot \frac{C(d_{me})}{C(d_b)} \tag{2}$$

where d_b and d_{me} are mobility diameter and mass equivalent diameter, while $C(d_b)$ and $C(d_{me})$ are the corresponding Cunningham slip correction factors. The slip correction factors are given by (Kulkarni, et al., 2011):

$$C(d_i) = 1 + \frac{2\lambda}{d_i}\left(1.142 + 0.558 \exp\left(-0.999 \frac{d_i}{2\lambda}\right)\right) \tag{3}$$

19

547 where λ is the mean free path of the gas molecules and d_i corresponds to either of d_{me} or d_b.
548 The mass equivalent diameter (d_{me}) was calculated using the following equation (Kelly and
549 McMurry, 1992):

550
$$d_{me} = \left(\frac{6m}{\pi\rho_p}\right)^{1/3} \qquad (4)$$

551 where ρ_p is the material density of the silica particle (see Table 1)

552   To calculate the volume and surface equivalent diameters (d_{ve} and d_{se}) of the silica
553 particles, which will be required to estimate the CCN capability of these particles, in addition
554 to the mobility and mass data, knowledge on the volume-based shape factor (χ') is also required
555 (see DeCarlo et al., 2004 and Kumar et al. 2011a for details):

556
$$\frac{d_{Ve}}{C(d_{Ve})} = \frac{d_b}{\chi . C(d_b)} \qquad (5)$$

557
$$d_{se} = \frac{3\chi d_{Ve} - d_b}{2} \qquad (6)$$

558 In this regard two limiting assumptions can be made. The first one is to assume compact
559 agglomerates with nearly spherical shape and internal voids. In this case the mobility and
560 volume equivalent diameters are approximately equal ($\chi'=1$) and also equal to the surface
561 equivalent diameter, but larger than the mass equivalent diameter, i.e. $d_b = d_{ve} = d_{se} > d_{me}$.
562 The particle density is in this case lower than the pure silica material density, but equal to the
563 effective density. The second assumption is to approximate the silica particles as chain-like
564 agglomerates with no internal voids, for which mass and volume equivalent diameters are equal
565 ($\chi = \chi'$), but smaller than surface equivalent and mobility diameters, i.e. $d_{ve} = d_{me} < d_{se}$ and
566 d_b. In this case the particle density would be the same as the pure silica material density but
567 higher than the effective density.

568   The fractal dimension (D_f) of the silica particles provides further insight on their
569 sphericity (Boldridge, 2010; DeCarlo et al., 2004; Keskinen et al., 2011): for perfect spheres
570 $D_f = 3$ and for line-like structures $D_f = 1$.

571   The fractal dimension of the pure silica particles was determined using the scaling law
572 for effective density versus mobility diameter (Skillas et al., 1998, 1999):

573
$$\rho_e \propto d_b^{(D_f-3)} \qquad (7)$$

574 , is particle bulk density andwhere ρ_e is the particle effective density. The effective density of
575 particles (ρ_e) was estimated using the following equation (Virtanen et al., 2004)(Kelly and
576 McMurry, 1992; Park et al., 2003a; Virtanen et al., 2004; Liu et al., 2012):

577 $\rho_e = m/(\pi d_b^3/6)\text{,}$ (3̶8)

578 where m is the mass of the particles determined ~~by~~ using APM (Eq. 1). ~~The mass equivalent~~

579 ~~diameter () was calculated by the following equation (Kelly and McMurry, 1992):~~

580 ~~= (4)~~

581 ~~where ρ_p is the material density of the silica particle (see Table 1)~~

582 ~~Slip correction factors are given by (Kulkarni, et al., 2011; Kumar et al., 2011b):~~

583 ~~$C = 1 +$ (5)~~

584 ~~where λ is the mean free path of the gas molecules and corresponds to either of or .~~

585 ~~The fractal dimension of the particles was determined using the scaling law for effective density~~

586 ~~versus mobility diameter (Skillas et al., 1998, 1999; Virtanen et al., 2004):~~

587 ~~$\propto$ (6)~~

588 ~~After estimating the shape factor of the aggregates, the volume equivalent diameter () and~~

589 ~~surface equivalent diameter of the particles were calculated using the following relations~~

590 ~~(DeCarlo et al., 2004; Kumar et al., 2011a):~~

591 ~~= (7)~~

592 ~~= (8)~~

593 ~~The effect of non-sphericity on CCN activation was accounted for by using the surface~~

594 ~~equivalent diameter (), instead of mobility diameter (), for pure and mixed silica particles. From~~

595 ~~here on we will thus use to denote the surface equivalent diameter.~~

596

3.2 CCN activation of soluble particles

598 κ-Köhler theory (Petters and Kreidenweis, 2007) was used to estimate the critical

599 supersaturation of pure ammonium sulphate, sucrose and BSA particles. The saturation ratio

600 (S) is expressed as:

601 $S = \dfrac{d_p^3 - d_{dry}^3}{d_p^3 - d_{dry}^3(1-\kappa)} \exp\left(\dfrac{4\sigma_w M_w}{RT\rho_w d_p}\right)$ (9)

602 where σ_w is the water surface tension, ρ_w is the water density, M_w is the molar mass of water, R

603 is the universal gas constant, T is the temperature, d_{dry} is the dry particle diameter, d_p is the

604 droplet diameter and κ is the hygroscopicity parameter of soluble particles.

605   The supersaturation (s) is equal to ($S-1$) and is expressed as a percentage. The maximum

606   value of the supersaturation is called critical supersaturation (s_c) – similar definition naturally

607   holding for critical saturation ratio S_c as well. Thus, at the critical point:

608     $$\frac{ds}{dd_p}\bigg|_{d_p=d_c} = 0 \qquad (10)$$

609   where d_c is called the critical diameter. The κ values for pure soluble particles were extracted

610   from previous studies or, in the case of BSA, derived by applying the following relation

611   introduced by Petters and Kreidenweis (2007) to our observations of the   critical

612   supersaturations of the pure soluble particles:

613     $$\kappa = \frac{4A^3}{27d_{dry}ln^2 S_c} \qquad (11)$$

614   where S_c is the saturation ratio at the critical point, $A=\frac{4\sigma M_w}{RT\rho_w}$, σ =0.072 J/m^2, T =298.15 K, M_w

615   =0.018 kg/mol and ρ_w=1000 kg/m^3.

616   The pure soluble particles were assumed to be compact and spherical, and thus the

617   mobility diameter was used as the d_{dry} in Eqs. 9-11.

618

619   **3.3 CCN activation of insoluble silica**

620   The critical supersaturation of pure silica particles was calculated using FHH adsorption theory

621   (Sorjamaa and Laaksonen, 2007, Kumar et al., 2009 and Kumar et al., 2011a). In this case the

622   relationship between water supersaturation s and particle size can be expressed as:

623     $$s = \frac{4\sigma_w M_w}{RT\rho_w d_p} - A_{FHH}\left(\frac{d_p-d_{dry}}{2d_{H_2 o}}\right)^{-B_{FHH}} \qquad (12)$$

624   where d_{H2O} ·(= 2.75 Å) is the diameter of the water molecule , and A_{FHH} and B_{FHH} are the FHH

625   adsorption isotherm parameters. The first and second terms on the right hand side of Eq. 12

626   correspond to the contributions from the Kelvin and adsorption effects, respectively.

627   In the literature, different values of the parameters A_{FHH} and B_{FHH} for silica particles have

628   been reported. Kumar et al. (2011a) obtained the values 2.95 and 1.36 for A_{FHH} and B_{FHH} of

629   quartz silica, respectively, and Keskinen et al. (2011) assigned values of 4.82 and 2.16 for A

630   and B for non-agglomerated fumed silica particles (Degussa, Aerosil-300) with the diameter of

631   8 and 10 nm.

632   To yield a reasonable estimate of the surface available for adsorption, the surface

633   equivalent diameter of the pure silica particles was used as d_{dry} in Eq. 12.

634

635   **3.4 CCN activation of mixed soluble and insoluble particles**

636   Kumar et al. (2011b) used adsorption activation theory assuming that the particles are spheres

637   and presented a shell and core model describing mixed particles with an insoluble and a soluble

638   fraction. the core consisting of insoluble dust, and the shell consisting of a layer of soluble salt.

639   They presumed that the soluble part coats the insoluble part and introduced the following

640   relation between water supersaturation, particle size and composition:

641    $$s = \frac{4\sigma_w M_w}{RT\rho_w d_p} - \frac{\varepsilon_s d_{dry}^3 \kappa}{(d_p^3 - \varepsilon_i d_{dry}^3)} - A_{FHH}\left(\frac{d_p - \varepsilon_i^{1/3} d_{dry}}{2 d_{H_2 o}}\right)^{-B_{FHH}}$$ (13)

642   where ε_i and $\varepsilon_s = 1 - \varepsilon_i$ are the insoluble and soluble volume fractions in the dry particles and κ

643   is the hygroscopicity parameter of the soluble part. A_{FHH} and B_{FHH} are the FHH adsorption

644   isotherm parameters of the insoluble part, which is assumed to interact with the water through

645   adsorption onto its surface.

646   To estimate the average insoluble volume fractions of the mixed particles, the following

647   relation was used:

648    $$\varepsilon_i = \frac{m_i/\rho_i}{m_i/\rho_i + m_s/\rho_s}$$ (14)

649   where m_i and m_s are the insoluble and soluble mass fractions in the total mixed aerosol

650   population, and ρ_i and ρ_s are the densities of the insoluble and soluble parts, respectively. The

651   bulk densities of the used components are listed in Table 1.

652   In the second term of Eq. 13 the volume equivalent diameter was used as d_{dry}, while the

653   surface equivalent diameter was assumed to represent the d_{dry} in the last term.

654

655   **4 Results and discussion**

656   **4.1 Particle size distributions**

657   The SMPS measurements yielded the average number size distributions for silica particles

658   mixed with $(NH_4)_2SO_4$, sucrose and BSA (Fig. 2). Figure 2a displays average number size

659   distributions for particles made of pure fumed silica, pure $(NH_4)_2SO_4$ and particles made of

silica and different amounts of $(NH_4)_2SO_4$. As is evident in the figure, size distributions of particles generated from pure silica or pure $(NH_4)_2SO_4$ are unimodal while size distributions of particles generated from the silica-$(NH_4)_2SO_4$ mixtures are bimodal. The mean mobility diameter is ~30 nm for the pure $(NH_4)_2SO_4$ particles, and approximately 150 nm for the pure silica particles. The first mode of the bimodal size distributions, associated with particles generated from the aqueous bulk mixtures, is centered at a diameter of less than 30 nm. The second mode, with lower number concentration, is centered at approximately 150 nm. Fig. 2b shows the average number size distributions of particles made of sucrose and silica. Particles made of pure sucrose have a mean diameter of approximately 50 nm. Size distributions associated with particles generated from the silica-sucrose mixtures are bimodal (Fig. 2b); the first mode centered at a diameter of less than 50 nm and the second mode centered at a diameter of about 150 nm. Similarly, Fig. 2c shows the average SMPS number size distributions of particles made of silica and BSA. These data are comparable with previous two measurements in Figs 2a-b. The particles made of the large BSA protein have a mean diameter of about 75 nm. The mode associated with particles made of a mixture of BSA and silica is centered at about 150 nm.

In the case of mixed aerosols, the particles in the first mode of the bimodal size distributions are likely pure soluble particles, while the second mode of the bimodal distribution curves represents silica particles mixed with soluble species. Hence, when analysing the activation behaviour of mixed particles we omitted the CCNc data of the smallest particles by subtracting their contribution from the CCN numbers and restricted our analysis to particle sizes larger than 100 nm.

~~In order t~~To estimate the average soluble volume (mass) fractions in the mixed particles, we calculated the ~~amount~~ fraction of soluble material lost to ~~in~~ the first pure mode of the particle size distributions and subtracted it from the total soluble mass. In this regard, we fitted log-normal distribution curves to the number size distributions associated with particles from the mixtures and estimated the volume and mass distributions related to each particle number size distribution. Hereupon, it was possible to estimate the fraction of total soluble mass remaining in the first mode of the bimodal size distributions for each mixture, and the fraction of the total soluble mass which was mixed with silica (Table 2). By multiplying this fraction with the soluble mass fraction in the bulk mixture we gained an estimate of the real average soluble mass fraction in the mixed/coated particles excluding the portion of the pure soluble particles. As is

692 evident from Table 2, the overall mass losses of the soluble materials from the first mode are

693 small, and 87-100% of the total soluble masses were mixed with silica particles.

694

695 **4.2 Mass analysis and size characterization of pure and mixed silica particles**

696 Since fumed silica particles are agglomerates, mass analysis of the pure silica particles could

697 help us to get a better understanding of their shape (see Sect. 3.1). Therefore, we estimated the

698 effective density and shape factor for these particles. As an example, Figure 3a shows the

699 observed average number concentrations of 100 nm size-selected silica particles (by DMA) for

700 different APM voltages. A log-normal distribution was fitted to provide the voltage value

701 corresponding to the peak of the distribution. After determining the mass of size selected

702 particles using Eq. 1, the effective density of the silica particles was estimated (Eq. 3). The

703 APM measurements were performed for two different rotation speeds of the APM (3000 and

704 5000 rpm). The achieved effective particle densities using these two rotation speeds are

705 presented in Fig. 3b. There is only a small difference in effective density between the two

706 different speeds, giving confidence in the results. Figure 3c displays the mass-based shape

707 factor (χ) of silica particles for different mobility diameters. χ is clearly larger than 1 and

708 increases by increasing mobility diameter. This indicates that internal voids and/or irregularities

709 of the particles increase with increasing particle diameter (Kelly and McMurry, 1992).

710 Afterward, tThe fractal dimension of the silica particles was estimated using the slopes

711 of the curves in Fig. 3b and Eq. 6. yielding D_f The slope values, of 2.54 and 2.55, for thewere

712 fitted respectively for of the silica particles in 3000 and 5000 rpm rotation speeds, thus

713 suggesting closer to spherical rather than rod- or chain-like structures. of the APM instrument.

714 Fitted The fitted D_f values are also close to the value (D_f=2.57) reported by Keskinen et al.

715 (2011) and Ibaseta and Biscans (2010) (D_f=2 to 2.5) for fumed silica (Degussa, Aerosil-300

716 and -200, respectively). We therefore expect the silica particles to be better represented by the

717 "compact agglomerates" assumption and applying this assumption (χ'=1, see Sect. 3.1), the

718 volume and surface equivalent diameters used in all the CCN activity calculations were thus

719 approximated with the mobility diameters. Figure 3c displays the dynamic shape factor of silica

720 particles for different mobility diameters. The shape factor of the silica particles increases by

721 increasing mobility diameter, which indicates that irregularities in particle shape or internal

722 voids within the particles increase with increasing particle diameter (Kelly and McMurry,

723 1992). By using the derived shape factors the surface equivalent diameter corresponding to

25

724 ~~different mobility diameters of silica particles (using Eq. 8) could be estimated (Fig. 3d). As~~
725 ~~expected, because of the void spaces inside the silica agglomerates, the surface equivalent~~
726 ~~diameter for silica particles is larger than its corresponding mobility diameter. The surface~~
727 ~~equivalent diameter was then used in all the theoretical calculations to represent the physical~~
728 ~~size of the particles in Eqs. 12-13.~~

729   The mass analysis results were only available for the pure silica particles. When analysing
730 the CCN activation data for the mixed particles, we assumed that the effective density of the
731 silica in the mixed particles was similar to the effective density of the pure silica particles. The
732 physical meaning of this assumption would be that the silica present in the mixed particles
733 would contain the same volume of voids per unit silica mass as the pure particles. Furthermore,
734 when calculating the critical supersaturations using Eq. 13 the adsorption term was calculated
735 using the surface equivalent diameter d_{se} as d_{dry} and the solubility term using the volume
736 equivalent diameter d_{ve} as d_{dry}, which in our case, by compact agglomerates assumption d_{ve}
737 $= d_{se} = d_b$.

738

4.3 CCN activation results

740 Before analysing the CCN activity of the generated particles, all the activation curves were
741 charge-corrected using the procedure introduced by Moore et al. (2010). The ratio of the
742 corrected CCN and CN (Condensation Nuclei, measured by CPC) time series thus determines
743 the activated fraction (also referred to as activation ratio) of the specified particles (Kumar et
744 al., 2011a). Furthermore, as described in Sec. 4.3.2, for the mixed particles the contributions of
745 the smaller completely soluble particle mode (see Fig. 2) were subtracted from the CCN
746 concentrations. Finally all the activation curves used in the further analysis were normalized
747 using a correction factor derived from the ammonium sulphate (AS) experiments, assuming that
748 AS activation probability reaches unity at high supersaturations. In the cases where the
749 normalization with the AS data would have produced CCN/CN values larger than unity, the
750 value was set to unity instead.

751

4.3.1 CCN behavior of pure components

753 Figure 4 shows the activation ratio dependence on supersaturation for 120 nm (mobility
754 diameter) pure silica, BSA, sucrose and ammonium sulphate particles. A sigmoid curve was
755 fitted to each set of activation ratio data. Critical supersaturation (s_c) is often associated with

756 the supersaturation where 50% of the particles are CCN activated – equivalent to a CCN/CN-
757 ratio of 50%, and we will follow this convention although the two are not necessarily equal
758 when the CCN/CN curve is not a step function. As expected, $(NH_4)_2SO_4$ particles, which are
759 the most hygroscopic particles investigated in this study (see κ values in Table 1), activated at
760 lower supersaturations than was the case for sucrose, silica and BSA particles. The pure silica
761 particles, which are insoluble and non-hygroscopic, exhibited the highest critical
762 supersaturation of the investigated compounds (Fig. 4).

763 Figure 5 displays activation ratio against supersaturation for pure silica particles of
764 different mobility diameters. As is evident from Fig. 5, the critical supersaturation decreases
765 with increasing particle diameter. Experimentally and theoretically determined critical
766 supersaturations of pure silica particles as a function of particle mobility diameter are shown in
767 Fig. 6. Previously, the values for FHH adsorption parameters (Eqs. 10 and 12) of different
768 types of silica have been determined by Kumar et al. (2011a) (quartz), and Keskinen et al.
769 (2011) (Fumed silica, Aerosil-300). To compare our results (Fumed silica, Aerosil-90) of the
770 pure silica activation to these studies, we fitted the FHH adsorption parameters for the pure
771 silica particles (Fumed silica, Aerosil-90). A_{FHH} and B_{FHH} values of 2.50 and 1.962 explain our
772 results on the activation diameter vs. critical supersaturation (Fig. 6), although the fits were
773 difficult to constrain uniquely. The results indicate, however, that oOur results are closer to
774 those reported by better in line with the work of Keskinen et al. (2011) than Kumar et al. (2011a)
775 –, but although the A_{FHH} and B_{FHH} values are close to those reported by Kumar et al. (2011a).
776 This highlights the sensitivity of the fits to these valuesadsorption parameters, reflecting the
777 fact that our data set is not sufficient for constraining any physical or chemical phenomena
778 behind these values. In particular, the parameter A_{FHH}, describing the interactions of the first
779 monolayer with the adsorbent surface, seems to be difficult to constrain based on the CCN
780 activation data. This is perhaps not surprising as at the point of activation the rapid condensation
781 of water might relatively soon destroy the information of the very first steps of the adsorption /
782 monolayer formation. For the parameter B_{FHH}, on the other hand, the fits seem to reproduce
783 relatively robust values. CCN activation measurements are probably not the best approach for
784 yielding accurate data of the physical phenomena behind the adsorption parameters – as a lot
785 of information has already been lost at the point where the CCN are activated and detected –
786 but should be rather regarded as a valuable source of information on the processes limiting
787 atmospheric cloud droplet formation. It must should also be pointed out that the quartz silica
788 (Kumar et al., 20092011a) is not as hydrophilic as fumed silica which probably affects the

789 critical supersaturation. Furthermore, the FHH adsorption parameters in Keskinen et al. (2011)
790 study were fitted for only 8 and 10 nm fumed silica particles which were most likely spherical
791 and thus potentially not fully representative of the agglomerated particles that we used. Impurity
792 of the silica could also affect the results even though the deionized water conditions were as
793 pure as possiblewas used in all studies. To conclude, the experimental results for s_c of pure
794 silica particles were in good agreement with theoretical calculations using FHH adsorption
795 isotherm and small deviations were only observed for larger diameters.

796 To estimate the critical supersaturations of pure soluble particles, κ-Köhler theory (Eqs.
797 9 and 10) was applied. Table 1 lists κ values of the soluble materials used in this study. The
798 ability for ammonium sulphate particles to act as CCN has been widely studied (e.g. Garland,
799 1969; Kreidenweis et al., 2005; Hiranuma et al., 2011), and here we employed the previously-
800 reported hygroscopicity (κ) values (Petters and Kreidenweis, 2007), given the relatively good
801 agreement between the κ value fitted to our results (0.78) and the literature values. The κ value
802 for pure sucrose was extracted from Ruehl et al. (2010), which was also in reasonable agreement
803 with the value 0.08 that best described our results. For the pure BSA particles κit was calculated
804 based on Eq. 11 using the CCN activation results of pure BSA particles in this study. The
805 experimentally and theoretically determined critical supersaturations for pure $(NH_4)_2SO_4$, BSA
806 and sucrose particles are shown in Fig. 7. Indeed, κ-Köhler theory results using the literature
807 values for the hygrscopicity parameter were in good agreement with the experimentally
808 determined critical supersaturations of pure soluble particles.

809

810 **4.3.2 CCN behavior of the mixtures**

811 Here we present the CCN activation results of co-synthesized silica particles mixed with
812 $(NH_4)_2SO_4$, sucrose or BSA considering the determined total soluble fractions in the mixed
813 particle population from Table 2.

814 The activation ratio curves were determined for different diameters of mixed particles
815 and different ratios of soluble to insoluble materials. For mixed particles the activation ratio
816 curves were modified by subtracting the contributions of the smaller completely soluble particle
817 from the CCN and CN concentrations using the following procedure: First, the contribution of
818 pure soluble particles to the total number of CN for each size were estimated by fitting two log-
819 normal modes to the size distributions such as those shown in Fig. 2. The pure soluble mode
820 was then subtracted from the CN data for each size to yield an estimate of the total numbers of

mixed CN. Second, using the CCN/CN ratios of the pure soluble particles (shown for 120 nm in Fig. 4) we could estimate the number of CCN originating from pure CN at each mobility diameter and supersaturation. Subtracting this from the total number of CCN, we could yield an estimate for the CCN/CN ratio for the mixed particles. Figure 8 ~~shows~~ represents the activation ratio curves for 150 nm (mobility diameter) pure and mixed particles. Although both the raw data (unnormalized) and the normalized curves are shown for completeness, only the normalized data was used in the follow-up analysis. It can be seen that the normalization procedure caused only very small adjustments to the 50% points inferred from the curves.

Figure 8a shows the activation probabilities of mixed silica-$(NH_4)_2SO_4$ particles. The critical supersaturation (corresponding to CCN/CN=50%) is higher for pure silica particles than for the particles with soluble material. Evidently, the pure $(NH_4)_2SO_4$ particles have the lowest critical supersaturation. Furthermore, the critical supersaturation decreases when the fraction of soluble material in the particles increases, and the CCN/CN curves are shallower (i.e. further from a step function) for the mixed as compared with the pure particles. The same behavior can be observed in Fig. 8b for 150 nm silica particles mixed with sucrose. Pure sucrose particles were activated at a supersaturation of 0.22% which is comparable to previous studies ~~of sucrose~~ (e.g. Rosenorn et al., 2006). s_c decreases with increasing sucrose ratio in the mixed particles, similar to what was observed for ammonium sulphate in Fig. 8a. In the case of particles containing BSA, however, a different behavior was observed: s_c was higher for particles made of 5% and 10% BSA than for particles made of pure silica (Fig. 8c). The reason for this behavior is not clear but it is known that adsorption of BSA on silica can affect the structural properties of BSA. As was explained by Larsericsdotter et al. (2005), for soft proteins such as BSA the structural stability decreases when adsorption onto other materials occurs. On the other hand, the BSA can also affect the agglomerate structure of the mixed particles – for instance through more compact agglomerates with increasing BSA concentrations (see e.g. Kiselev et al., 2010 and Stratmann et al., 2010 for discussion on effects of coating on agglomerate compactness). However, it is also possible that this effect is solely due to different distribution of the soluble materials as a function of particle size for the different bulk solution compositions, which is discussed in detail below.

To estimate the soluble mass fractions (ω_ss) in the coated/mixed particles required for the application of Eq. 13, the total amount of soluble ~~coating~~ material was first estimated by fitting log-normal size distributions to the observed size distributions (Sect. 4.1). The dashed lines in Fig. 9 show the theoretical critical supersaturations (using Eq. 13) of particles consisting of a

854   mixture of silica and ammonium sulphate assuming soluble volume fractions (ε_ss)

855   corresponding to these constant ω_ss (see Table 2 and the dashed lines of the insert in

856   Fig. 9) with changing diameter. These theoretical values of critical supersaturations are mostly

857   lower than the observed critical supersaturations (stars), and the size-dependence of the critical

858   supersaturation is not captured by the theory. We observed the same (although less pronounced)

859   behavior for silica particles mixed with sucrose and BSA (Figs. 10 and 11). In all three cases,

860   the observed critical supersaturations were higher than expected from the ~~shell-core~~ model by

861   Kumar et al. (2011b) using constant soluble mass fractions. The calculations are very sensitive

862   to the κ values and the deviation between experimental and estimated s_c for mixed particles

863   increases with increasing hygroscopicity. The largest deviations were observed for particles

864   mixed with $(NH_4)_2SO_4$, which is more hygroscopic (κ=0.61) than the other compounds, and the

865   smallest deviations were observed for silica particles mixed with BSA which has the lowest

866   hygroscopicity (κ=0.01). The adsorption term contribution to the critical supersaturation in Eq.

867   13 was generally minor: <0.72% for silica + $(NH_4)_2SO_4$, <3.8% for silica + sucrose and~~-~~ <7%

868   for silica + BSA of the total (~~kelvin~~ Kelvin + solubility + adsorption) contribution for all the

869   studied compositions and supersaturations. The theoretical predictions were thus dominated by

870   the Kelvin and solubility effects – similarly to the case of soot agglomerates studied by Henning

871   et al (2010).

872   The small contribution of the adsorption term to the theoretical predictions combined with

873   the shallow activation ratio curves (see Fig. 8) suggest that the reason for the apparent

874   discrepancy between the theoretical and the observed critical supersaturations is a non-constant

875   distribution of the soluble material with varying particle size. This explanation seems

876   particularly feasible taking into account the good agreement between the experiments and

877   theory for the pure particles, and the fact that the particle generation method (atomization and

878   drying of aqueous solutions) does not allow for controlling the ratio of soluble to insoluble

879   materials at a given particle size – only for the overall aerosol population. To yield further

880   insight into this, we estimated the distribution of the soluble material by fitting size-dependent

881   ε_s distributions to the CCN/CN vs. s_c curves (e.g. Fig. 8) using Eq. 13 – thus assuming that all

882   the mixed particles that activate at a given supersaturation interval contain a specific soluble

883   volume (mass) fraction. It is worthwhile to note that the ε_s determined this way correspond to

884   the surface or volume equivalent diameters (linked to the particle mass~~volume equivalent~~

885   ~~diameter~~ through the modified silica ~~effective~~ density including internal voids, see Sect. 3), and

886   is thus not directly comparable to the mass fractions in the atomized solution.

887   The s_c (defined as the 50% point in the CCN/CN curves) vs. mobility diameter results

888   obtained through the fitting procedure are shown by the solid lines in Figs. 9-11, and the

889   resulting soluble mass fractions ω_ss corresponding to the ε_ss fitted to the 50% points in the

890   CCN/CN curves as a function of particle size are shown as the solid lines in the insets. The

891   results suggest a very uneven distribution of the soluble material as a function of particle size:

892   the small particles contain considerably higher fractions of soluble material than the larger ones,

893   and the effect increases with the amount of soluble material. In the case of BSA (Fig. 11), the

894   different mixture compositions lie relatively close to each other in terms of their critical

895   supersaturations – making it difficult to constrain the soluble contents of these particles.

896   However, it seems clear that at the small particle sizes (< 150 nm) the particle population is

897   dominated by pure BSA particles. At sizes between 150 and 250 nm, on the other hand,

898   extremely low BSA-content is required to reproduce the observed critical supersaturations. This

899   is of course also visible in Fig. 8c, where the mixtures with low BSA-content seem to activate

900   at even higher supersaturations than pure silica. The exact reason for this is not clear, but the

901   effect of BSA on silica particle structure (e.g. density etc.) could be speculated upon.

902   , there even appears to be a large number of pure BSA particles present at the low end of the

903   "mixed" size distribution governing the 50% activation point.

904   While the size-dependent ω_s shown in Figs. 9-11 correspond to the points at which 50%

905   of the CN activate as CCN for a given particle diameter and supersaturation, the ω_s values vary

906   even for a given particle size – as indicated by non-step function shape of the activation curves

907   in Fig. 8. An example distribution of the soluble mass as deduced from the CCN/CN vs. s_c data

908   (Fig. 8) using Eq. 13 is shown in Fig. 12 for the 150 nm mobility diameter mixed particles. The

909   figure shows that for each mixture, there is an uneven distribution of soluble mass fraction in

910   the particles of a given size (here 150 nm). In all cases, there are is a large amount number of

911   particles with very low soluble mass fractions (less than initial bulk solution) and the

912   composition of the size-selected particles is not constant. Similar conclusions were drawn by

913   Dusek et al. (2006) for soot particles coated by NaCl. When compared to the mass fractions in

914   the atomized solution, it can be seen that only in the case of sucrose the distribution peaks at

915   soluble mass fractions similar to the original solution, while the mixtures containing ammonium

916   sulphate and BSA have widely varying compositions.

917

918

5 Summary and conclusions

In this study, the CCN activation of pure and mixed particles of silica and soluble compounds (AS, sucrose and BSA) was investigated. Furthermore, the morphology and effective density of silica particles were investigated based on APM measurements. In addition, size distributions of the sampled particles were measured using a SMPS. Then non-sphericity of the particles was investigated by applying APM measurements and estimating mass-based dynamic shape factors and fractal dimensions of pure silica particles. Assuming that our pure and mixed silica particles are compact agglomerates, which is the most reasonable assumption for our silica particles with fractal dimension of 2.54-2.55 close to the spherical particles with fractal dimension of three, ~~By using these derived shape factors,~~ the surface and volume equivalent diameter~~s~~ ~~corresponding to different~~become identical to the mobility diameter~~s~~ of th~~e silica~~ese particles~~, which was needed for the theoretical calculations, was estimated~~. The SMPS results showed that the particles generated from pure compounds resulted in unimodal size distributions, while the particles generated from mixtures were associated with bimodal size distributions. The first peak of the bimodal size distribution indicated that also the mixture generated some pure soluble particles. The size distributions allowed us to estimate the total soluble vs. insoluble mass fractions present in the mixed particle population.

CCN activity measurements were conducted in various supersaturations up to 1.5%, and activation ratio curves were determined for the evaluated particles. Afterward, the experimental data were compared to theoretical values using adsorption theory (e.g. Sorjamaa and Laaksonen, 2007) for the pure silica particles, κ-Köhler-theory (Petters and Kreidenweis, 2007) for the pure soluble particles, and a ~~shell and core~~ model describing mixtures of soluble and insoluble components introduced by Kumar et al. (2011b)~~ for the mixed particles~~. The CCN activation of pure soluble and insoluble particles was in good agreement with κ-Köhler theory and adsorption theory. For mixed particles, however, the observed critical supersaturations were higher than those expected from the ~~shell and core~~ model by Kumar et al. (2011b), if constant soluble and insoluble mass fractions were assumed for the whole mixed particle population. This indicates that the particles were less hygroscopic than expected, indicating an uneven distribution of the soluble material in the aerosol size distribution. As the calculations were governed by the soluble mass (volume) fraction in the particles instead of adsorption effects, we could use the experimental critical supersaturations to estimate size-dependent distribution of the soluble material in the mixed particles. For particles > 150 nm in mobility diameter the soluble fractions were smaller and for particles < 150 nm mostly larger than in the

952 total mixed particle population – indicating that the soluble material preferentially accumulated
953 to particles < 150 nm, independent of the exact identity of the soluble species. If the uneven
954 distribution of the soluble material was accounted for, the framework by Kumar et al. (2011b)
955 could be successfully used to describe the CCN activation of insoluble particles mixed with
956 soluble pollutants.

957   Our results indicate that knowing the fraction of soluble material (instead of the
958 adsorption properties of the surfaces) is the key prerequisite for describing the CCN activation
959 of silica mixed with soluble pollutants – at least for the relatively large soluble fractions studied
960 here. ~~Our mixed particles consistent of varying soluble fractions, thus probably representing an~~
961 ~~aerosol population with various degrees of aging in the atmosphere.~~ Furthermore, our results
962 indicate that well-defined descriptions of the coating processes are crucial for elucidating the
963 phenomena governing the CCN activation of insoluble particles mixed with soluble
964 compounds. We also conclude that although the model by Kumar et al. (2011b) was originally
965 introduced for fresh dust coated by a layer of soluble salt after ageing, it gives a reasonable
966 estimate of the potential importance of adsorption as compared with the bulk solubility of the
967 mixed soluble-insoluble particles.
968

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974

975 **References**

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1128   doi:10.1080/02786820490445155, 2004.

1129

1130

1131   Table 1: Thermodynamic properties of components used in this study.

	Molar mass (g/mol)	Density (g/cm^3)	Solubility in water (Mass%)	κ
(NH$_4$)$_2$SO$_4$	132.14[a]	1.77[a]	43.3[a]	0.61[e]
Sucrose	342.3[a]	1.58[a]	67.1[a]	0.084[f]
BSA	66500[b]	1.362[b]	60[d]	0.013[g]
SiO$_2$	60.08[a]	2.16[c]	-	-

1132   [a] Haynes et al. (2013)

1133   [b] Mikhailov et al. (2004)

1134   [c] Grayson (1985)

1135   [d] Shiraiwa et al. (2011)

1136   [e] Petters and Kreidenweis (2007)

1137   [f] Ruehl et al. (2010)

1138   [g] This work

1139

1140 Table 2: The total soluble fraction of the solute masses in the bulk mixtures, the fraction of total
1141 soluble mass mixed with silica, the average soluble mass fraction of the mixed particles
1142 (calculated from particle size distributions, see text for details).

Soluble mass fraction in the bulk mixture (%)	Fraction of total soluble mass mixed with silica (%)			Total soluble mass fraction in the mixed particles (%)		
	Silica+ $(NH_4)_2SO_4$	Silica+ sucrose	Silica+ BSA	Silica+ $(NH_4)_2SO_4$	Silica+ sucrose	Silica+ BSA
25	92	98	87	23.4	24.6	22.5
10	88	99	99	8.9	9.9	9.9
5	87	99	~100	4.4	4.9	~5

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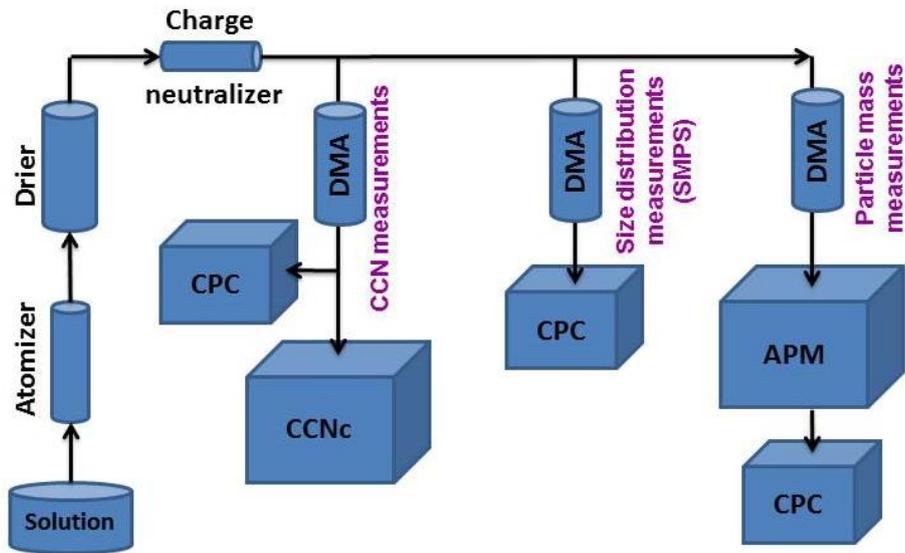
1146

1147 Fig. 1: Schematic of the experimental set up and three types of measurements: CCN activity

1148 measurements, size distribution measurements by SMPS and particle mass analyzing by APM.

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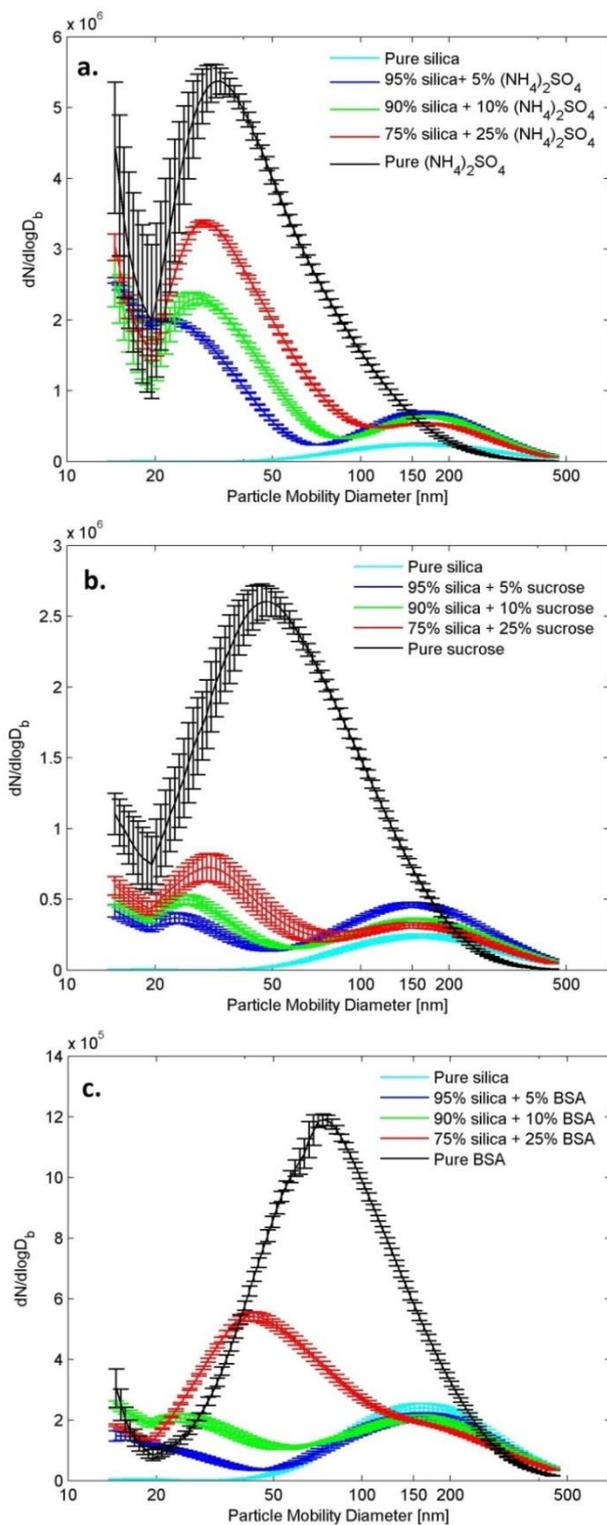
1150

1151 Fig. 2: Average particle number size distributions (SMPS) for silica particles mixed with **(a)**

1152 (NH$_4$)$_2$SO$_4$, **(b)** sucrose and **(c)** BSA. Each average size distribution is based on at least 70

1153 individual size distributions, and the error bars represent the standard deviation of the

1154 measurements.

a.

V_{APM} = 35 V

140
120
100
80
60
40
20
0

Number Concentration (dN/dlogD$_b$)

■ Experimental data
— Fitted curve

0   50   100   150

APM Voltage [V]

b.

1200
1100
1000
900
800
700
600
500

Particle Density [kg/m³]

Slope = D$_f$ - 3

Slope = D$_f$ - 3

□ ω = 3000 rpm, D$_f$ = 2.54
● ω = 5000 rpm, D$_f$ = 2.55

80   100   120   150   200   250   300

Particle Mobility Diameter [nm]

c.

1.9
1.8
1.7
1.6
1.5
1.4

Dynamic Shape Factor (χ)

χ = 0.636 log (d$_b$) + 0.251

■ Theoretical values
— Fitted curve

80 100   150   200   250   300

Particle Mobility Diameter [nm]

d.

400
350
300
250
200
150
100
50

Surface Equivalent Diameter [nm]

● Theoretical values
— Fitted line

50   100   150   200   250   300

Particle Mobility Diameter [nm]

1155

43

Fig. 3: **(a)** Average number concentration of 100 nm (mobility size) pure silica particles downstream the APM and at a rotation speed of the APM of 3000 rpm. The number concentrations were averaged over one minute for each APM voltage, and the error bars represent the standard deviation of about 60 measurements recorded under the same conditions. **(b)** ~~Density~~ Effective density of silica particles for different mobility diameters and two different rotation speeds of the APM (3000 and 5000 rpm). The fitted fractal dimensions are 2.54 and 2.55, respectively. **(c)** ~~Dynamic~~ Mass-based shape factor versus electrical mobility diameter for silica particles~~, (d) Theoretical surface equivalent diameter against mobility diameter of the silica particles~~.

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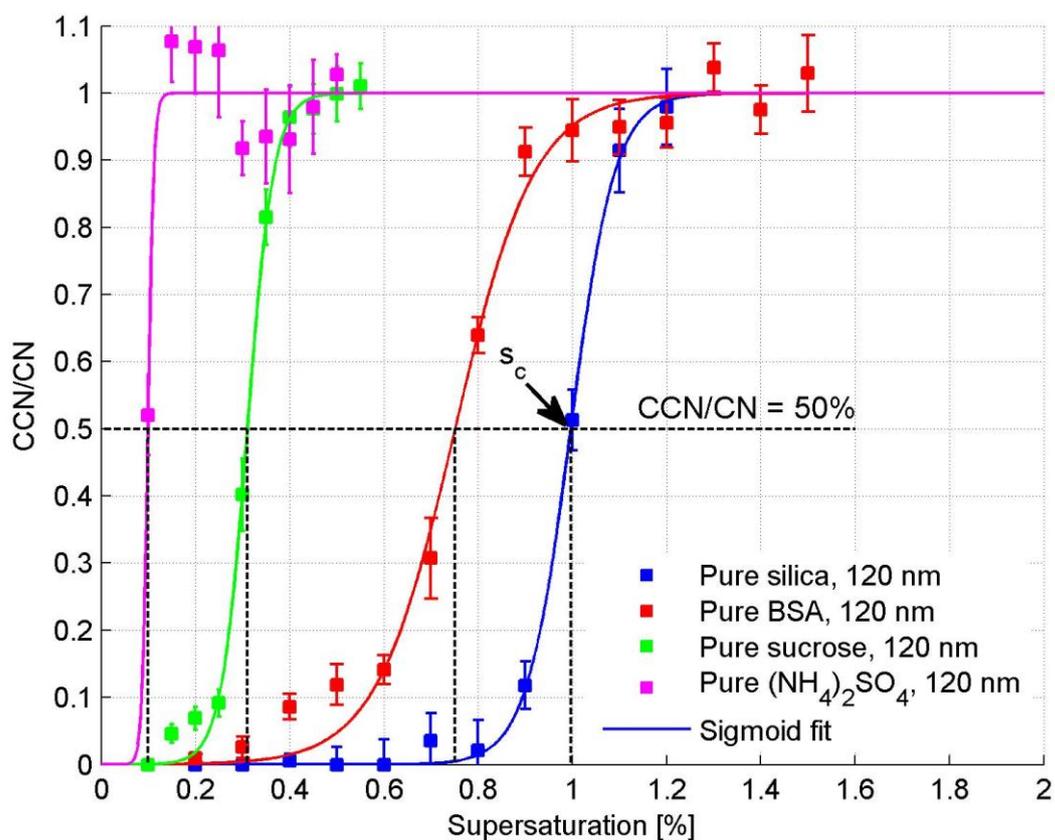
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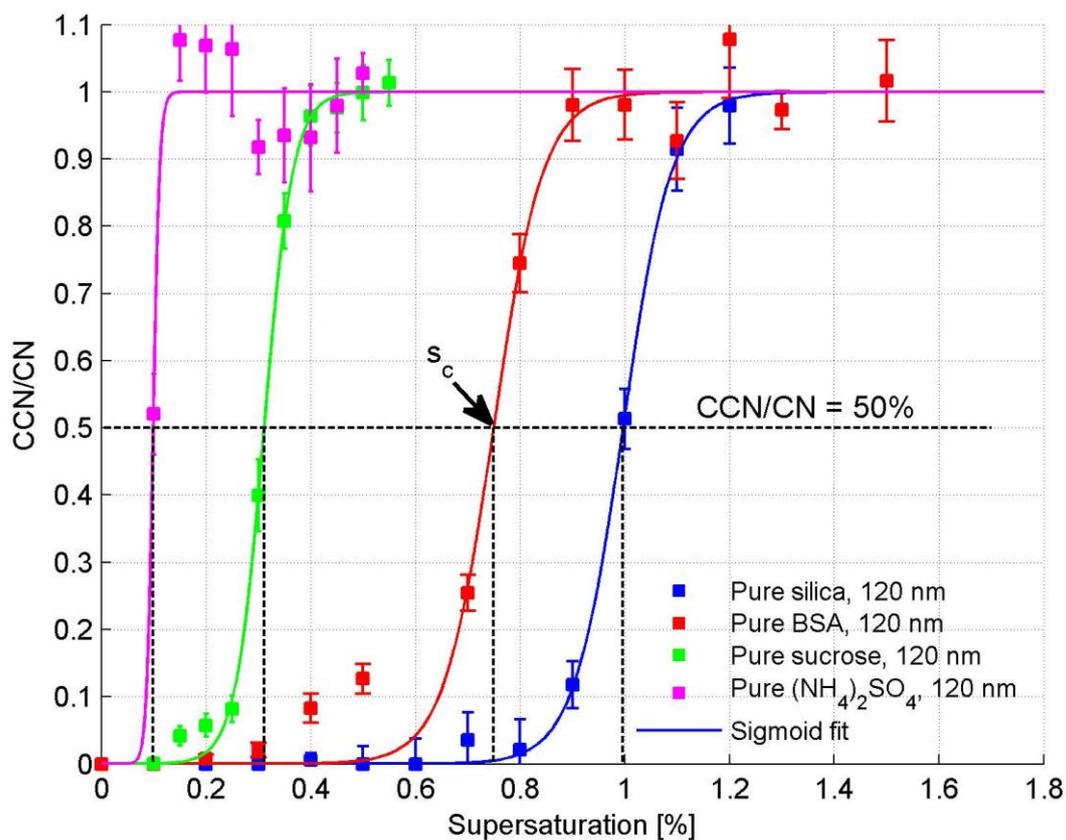
1168

1169   Fig. 4: The average activation ratio of pure soluble or insoluble particles with the mobility

1170   diameter of 120 nm at different supersaturations. Error bars represent the standard deviation

1171   of the activation efficiency of about 20 measurements corresponding to each supersaturation

1172   of the instrument. Critical supersaturation s_c is defined as the point where the activation ratio

1173   is equal to 50%.

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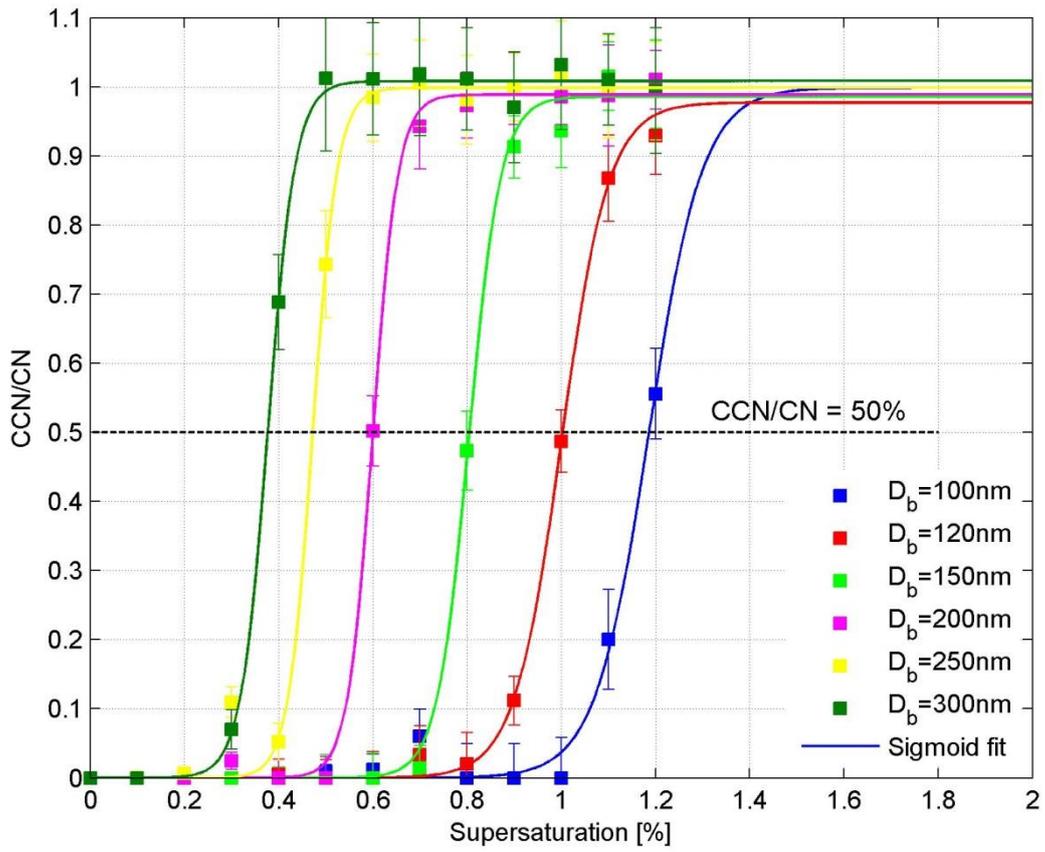
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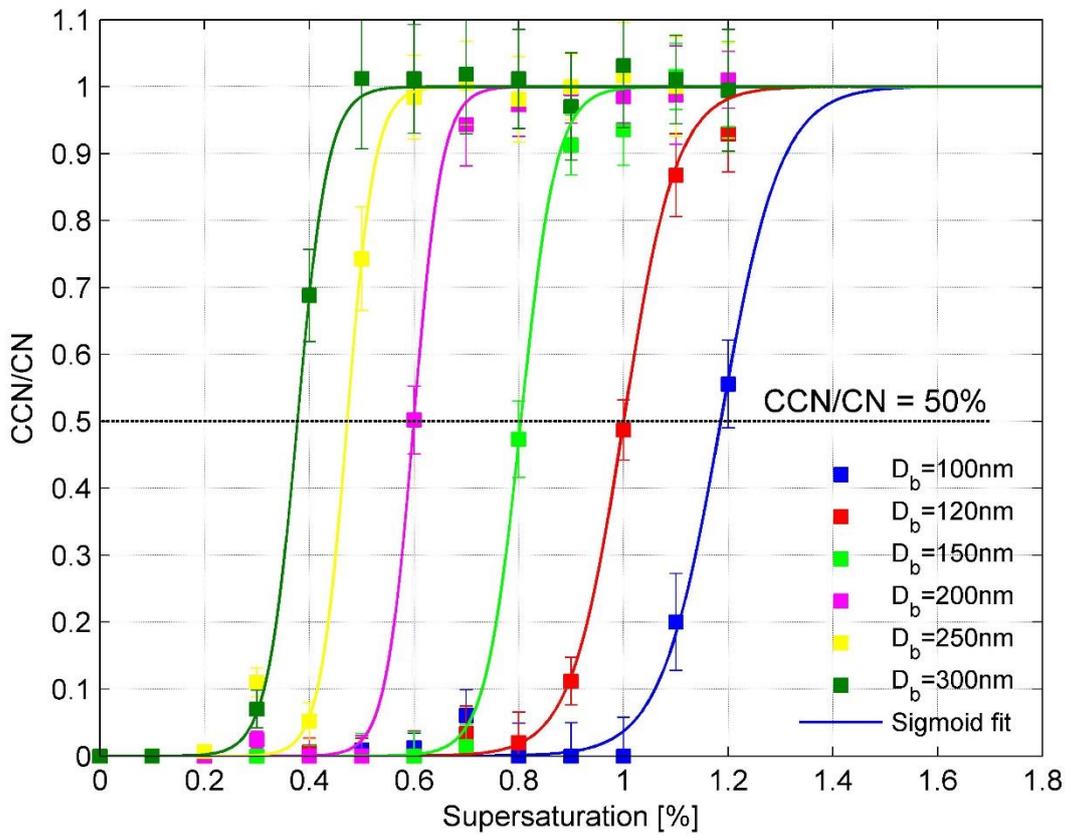
1176

1177   Fig. 5: The average activation ratio versus supersaturation for different mobility diameters of

1178   silica particles. Error bars represent the standard deviation of the measured activation efficiency

1179   as a result of about 20 measurements corresponding to each supersaturation of the instrument.

1180
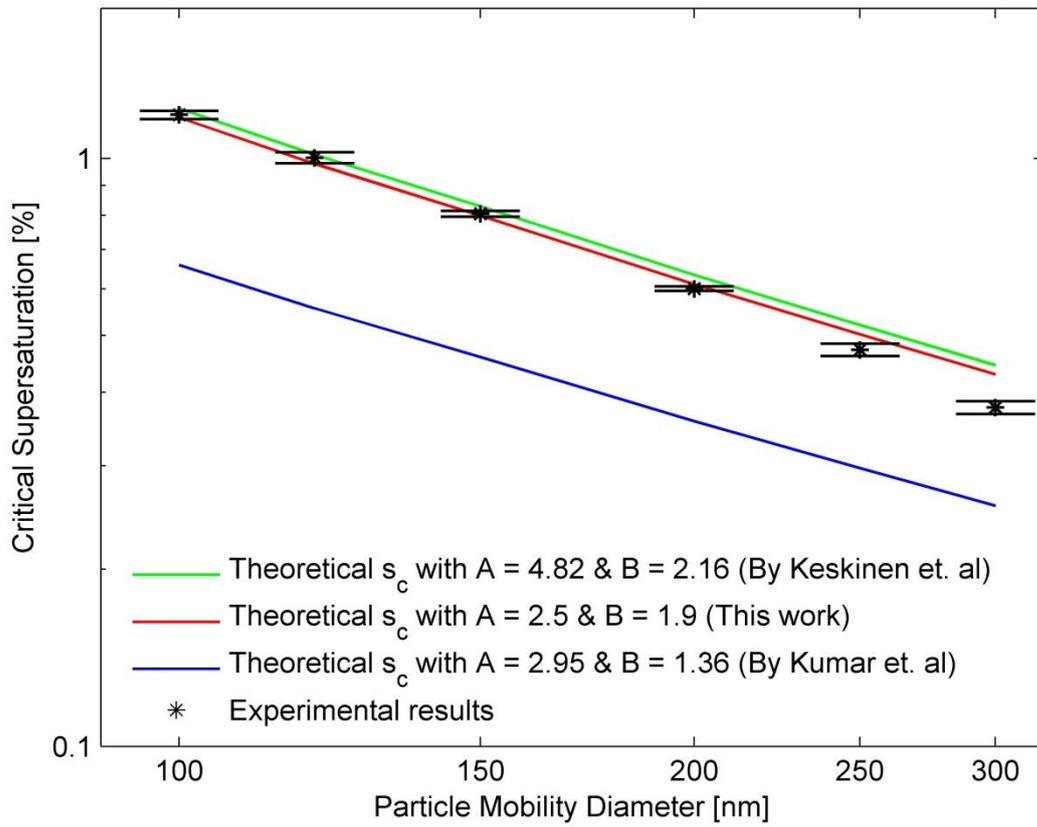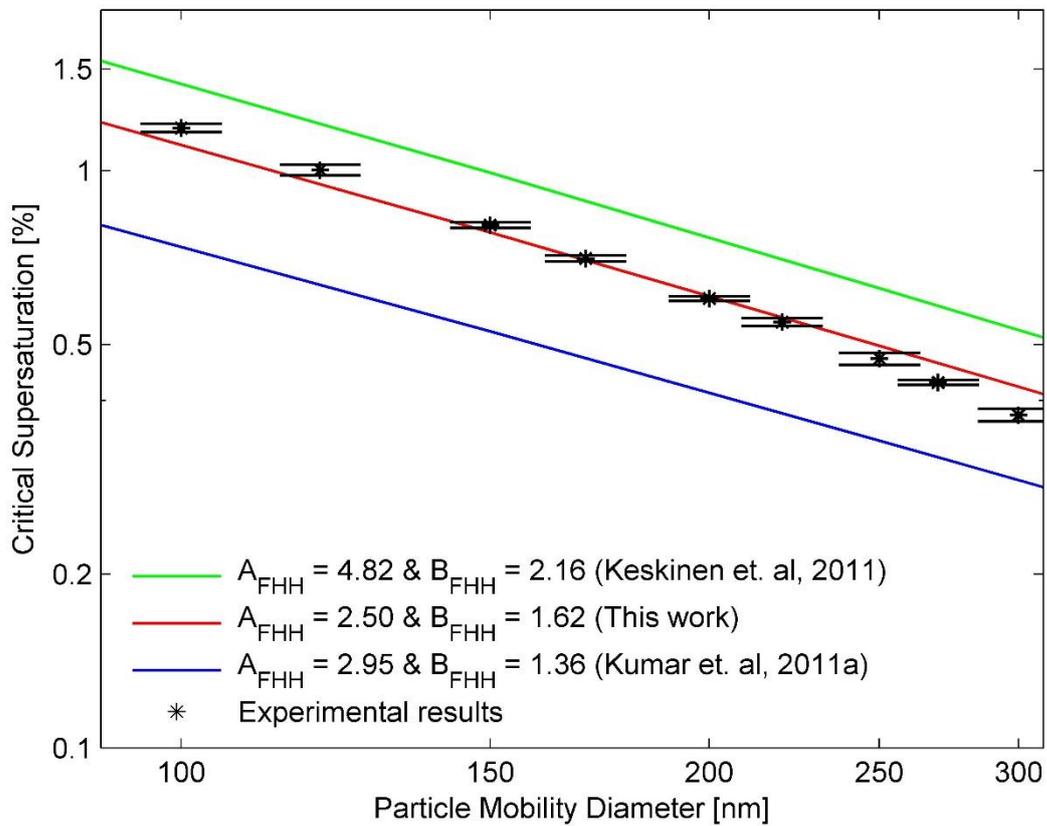
1183   Fig. 6: Critical supersaturations against activation mobility diameter of pure silica particles with

1184   different FHH adsorption isotherm parameters from different studies compared to experimental

1185   results. Error bars represent the minimum vs. maximum values of supersaturation to estimate

1186   the s_c corresponding to each d_b .

1187

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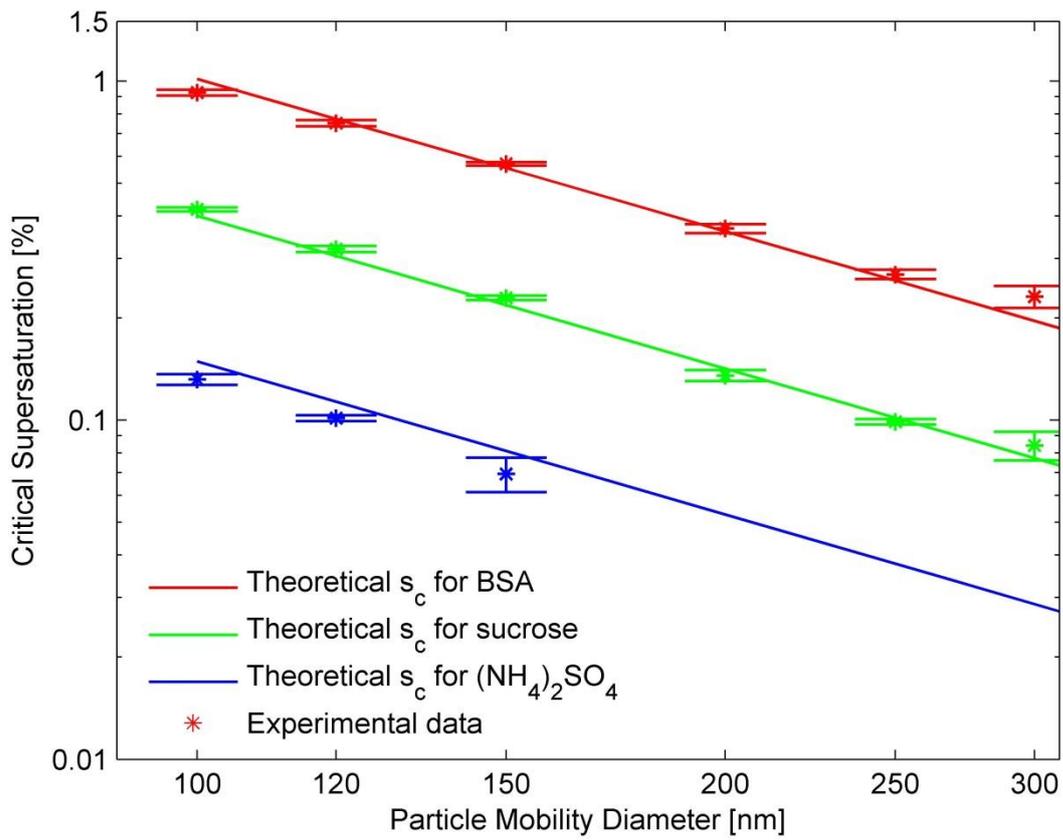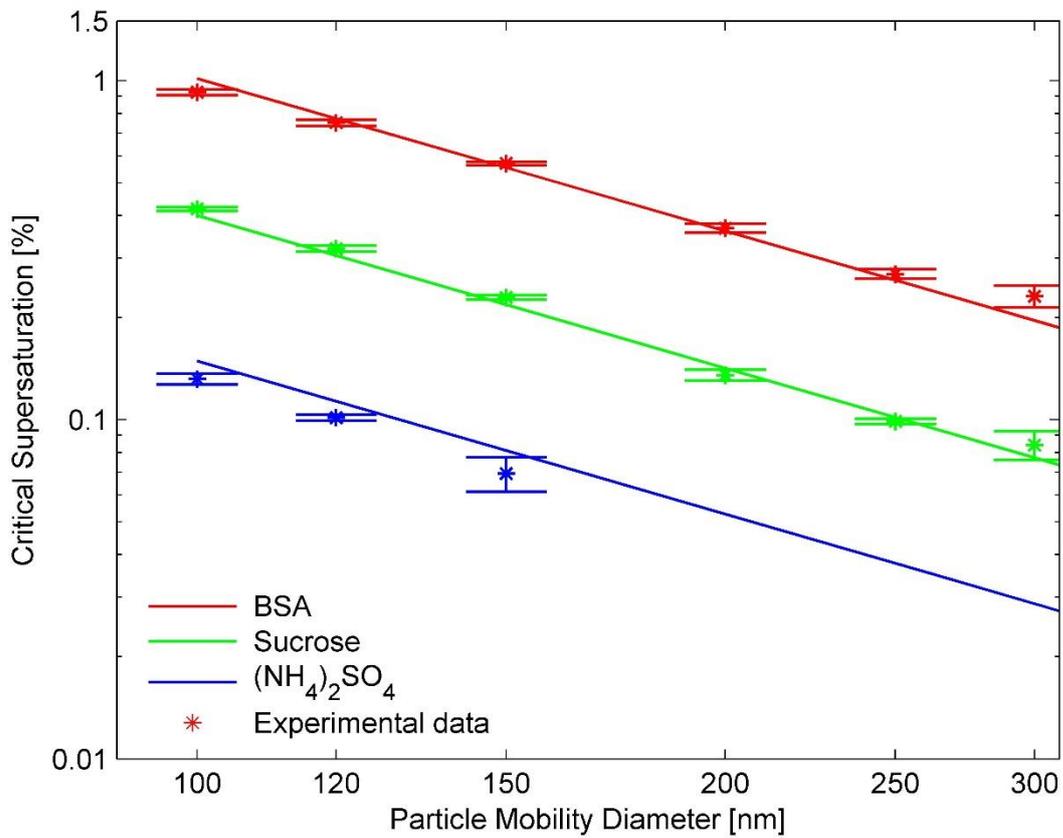
1191   Fig. 7: Experimental and theoretical critical supersaturations of pure $(NH_4)_2SO_4$, sucrose and

1192   BSA particles for different mobility diameters based on κ-Köhler theory. Error bars represent

1193   the minimum vs. maximum values of supersaturation to estimate the s_c corresponding to each

1194 d_b.

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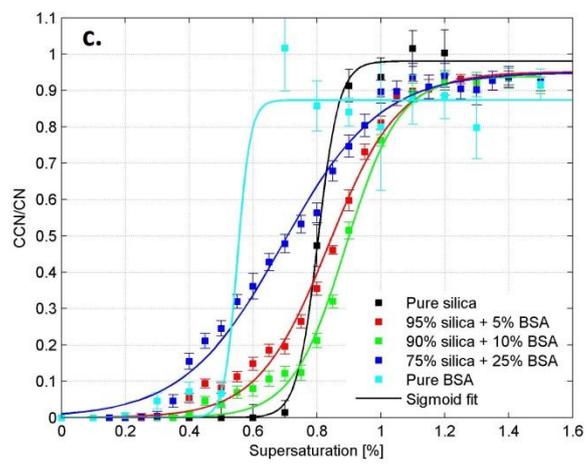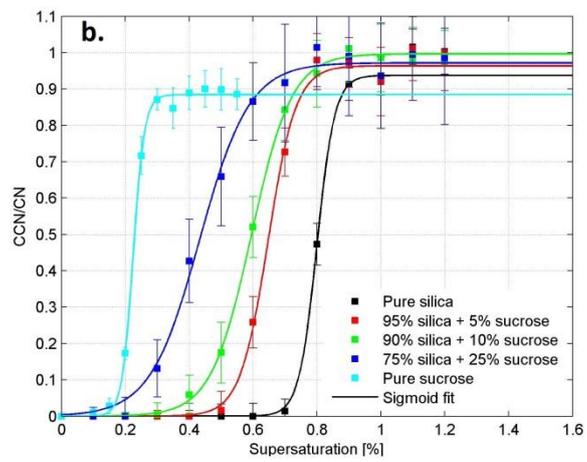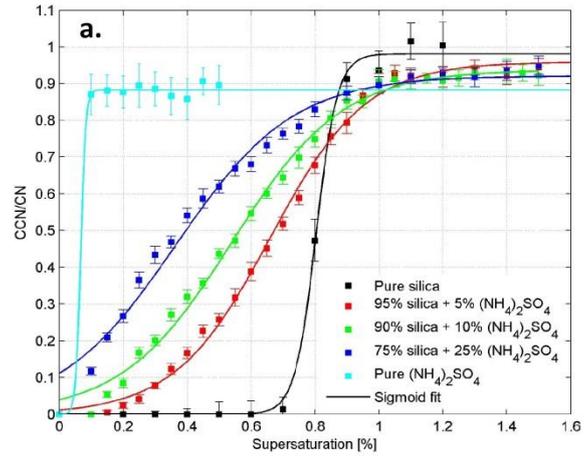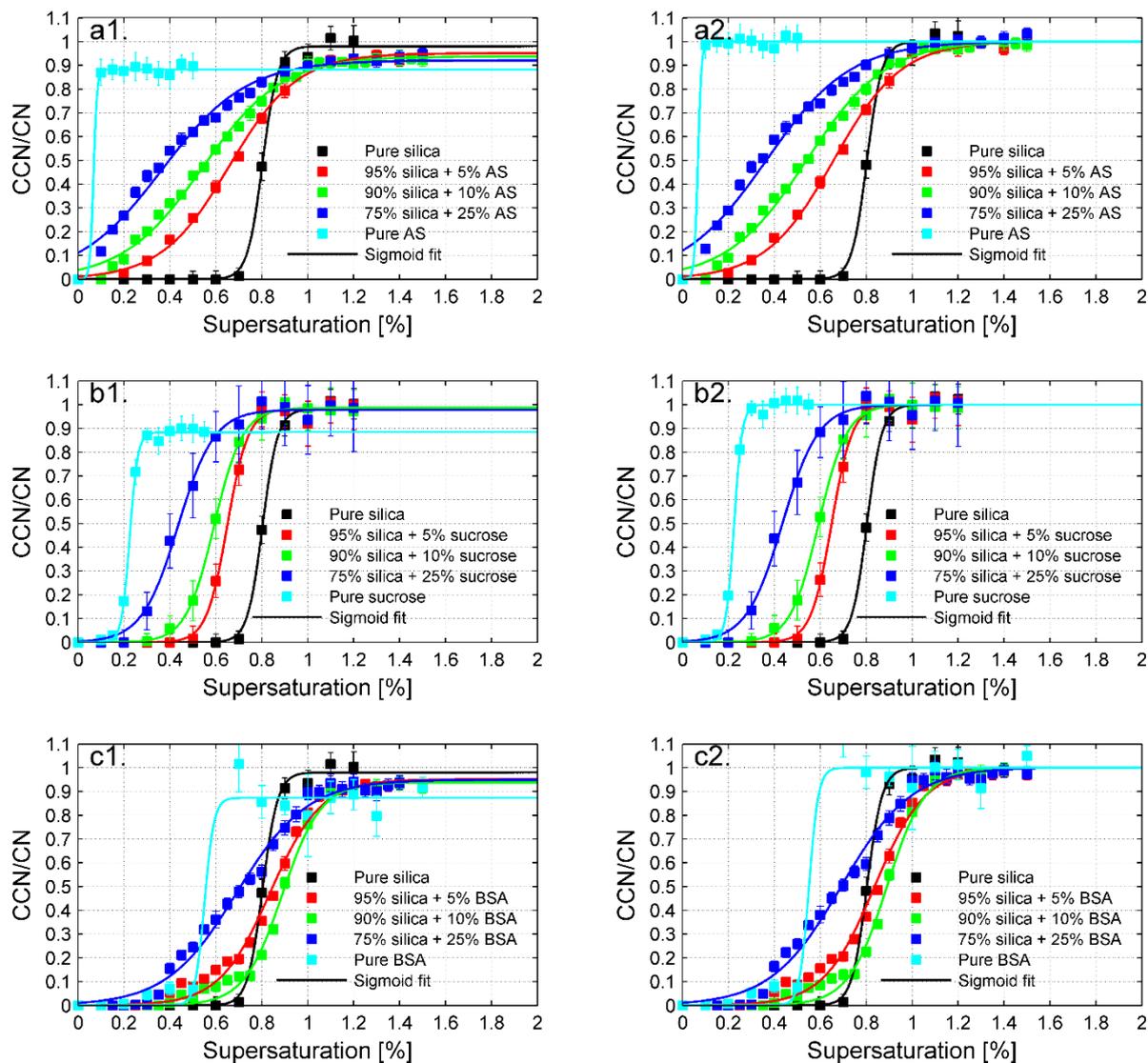
Fig. 8: (a) Activation ratio curves for different supersaturations of silica + (NH$_4$)$_2$SO$_4$ particles of 150 nm mobility diameter, (b) Activation ratio curves for different supersaturations of silica + sucrose particles of 150 nm mobility diameter, (c) Activation ratio curves for different supersaturations of silica + BSA particles of 150 nm mobility diameter. The activation curves on the left side (subplots a1-c1) represent the unnormalized data, while the activation curves on the right side (subplots a2-c2) show the normalized ones. Error bars represent the standard deviation of the measured activation efficiency as a result of about 20 measurements corresponding to each supersaturation of the instrument.

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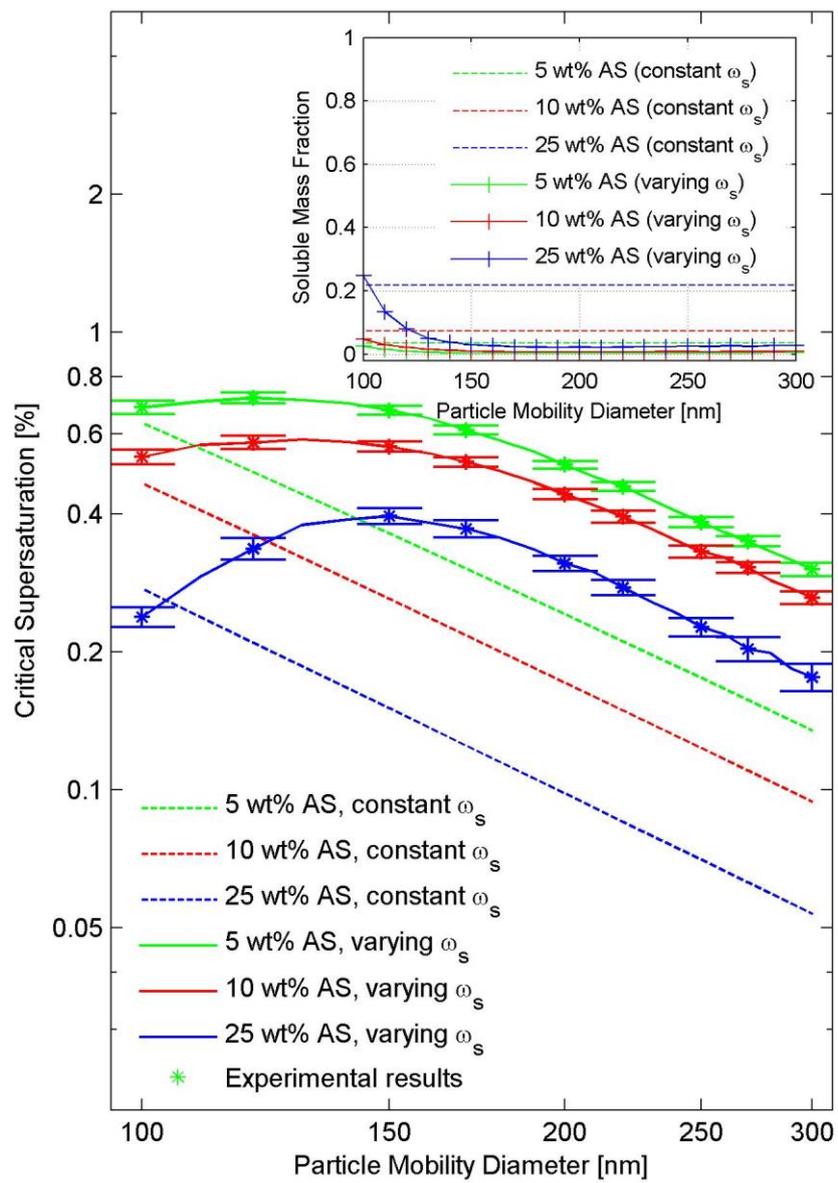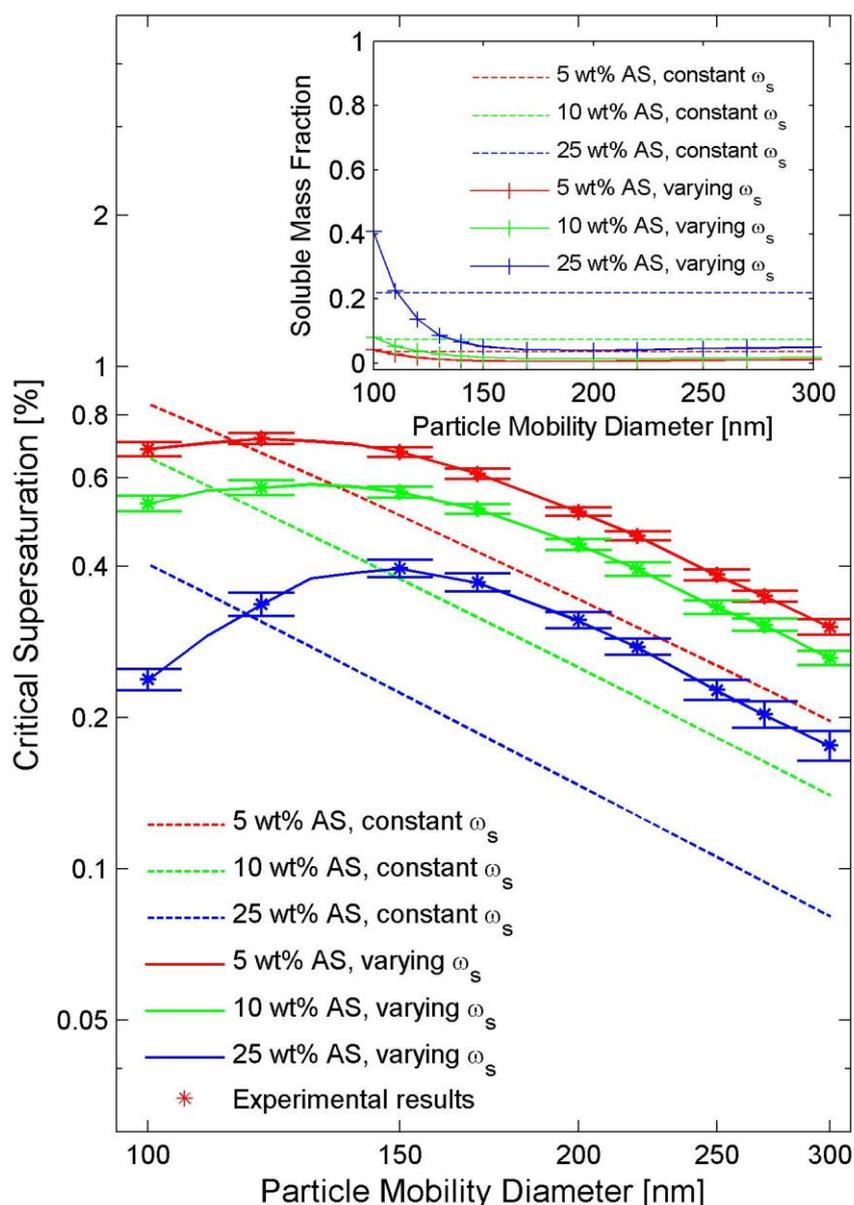
Fig. 9: Experimental and theoretical critical supersaturations for mixed silica + $(NH_4)_2SO_4$ (AS) particles for different particle mobility diameters using ~~theshell and core~~ the model by Kumar et al. (2011b). Dashed lines represent calculated critical supersaturations based on an assumption of constant soluble mass fractions (ω_s) with changing diameter and solid lines show the critical supersaturations based on the size-dependent soluble mass fractions. Error bars represent the minimum vs. maximum values of supersaturation to estimate the s_c corresponding to each mobility diameter. The inset represents assumed constant soluble mass fractions as well as size-dependent ones corresponding to the 50% points in the CCN/CN curves for different size vs. supersaturation pairs of mixed silica + $(NH_4)_2SO_4$ particles.

Fig. 10: Experimental and theoretical critical supersaturations for mixed silica + sucrose particles for different particle mobility diameters using ~~shell and core~~the model by Kumar et al. (2011b). Dashed lines represent calculated critical supersaturations based on an assumption of constant soluble mass fractions (ω_s) with changing diameter and solid lines show the critical supersaturations based on the size-dependent soluble mass fractions. Error bars represent the minimum vs. maximum values of supersaturation to estimate the s_c corresponding to each mobility diameter. The inset represents assumed constant soluble mass fractions as well as size-dependent ones corresponding to the 50% points in the CCN/CN curves for different size vs. supersaturation pairs of mixed silica + sucrose particles.

1231

Fig. 11: Experimental and theoretical critical supersaturations for mixed silica + BSA particles for different particle mobility diameters using ~~shell and core~~the model by Kumar et al. (2011b). Dashed lines represent calculated critical supersaturations based on an assumption of constant soluble mass fractions (ω_s) with changing diameter and solid lines show the critical supersaturations based on the size-dependent soluble mass fractions. Error bars represent the minimum vs. maximum values of supersaturation to estimate the s_c corresponding to each mobility diameter. The inset represents assumed constant soluble mass fractions as well as size-dependent ones corresponding to the 50% points in the CCN/CN curves for different size vs. supersaturation pairs of mixed silica + BSA particles.

Fig. 12: The distribution of soluble material on 150 nm (mobility diameter) particles in the mixed particles made of **(a1-3)** silica + $(NH_4)_2SO_4$ (AS), **(b1-3)** silica + sucrose, **(c1-3)** silica + BSA. Note that the smallest solubility bin extends down to zero, i.e. particles consisting of pure silica.