

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 will add 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 will

not change any of the conclusions of the manuscript but will change some of the absolute numbers to some extent, as illustrated in Figs. R1-R4 below.

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

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

- 1) *Assuming the silica particles are compact agglomerates having nearly spherical shape but internal voids. In this case the mobility (d_b) and volume equivalent diameters (d_{ve}) are approximately the same and also equal to surface equivalent diameter (d_{se}), but larger than the mass equivalent diameter (d_{me}) i.e. $d_b = d_{ve} = d_{se} > d_{me}$. The particle density is in this case lower than the pure silica material density (DeCarlo et al., 2004), but equal to the effective density.*
- 2) *Considering the silica particles as chain-like agglomerates with no internal voids, for which mass and volume equivalent diameters are equal (DeCarlo et al., 2004), but smaller than surface equivalent and mobility diameters, i.e. $d_{ve} = d_{me} < d_{se}$ and d_b . In this case the particle density would be the same as the pure silica material density but higher than the effective density.*

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

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

the data throughout the revised manuscript (i.e. just present the predictions corresponding to the solid lines in the revised manuscript).

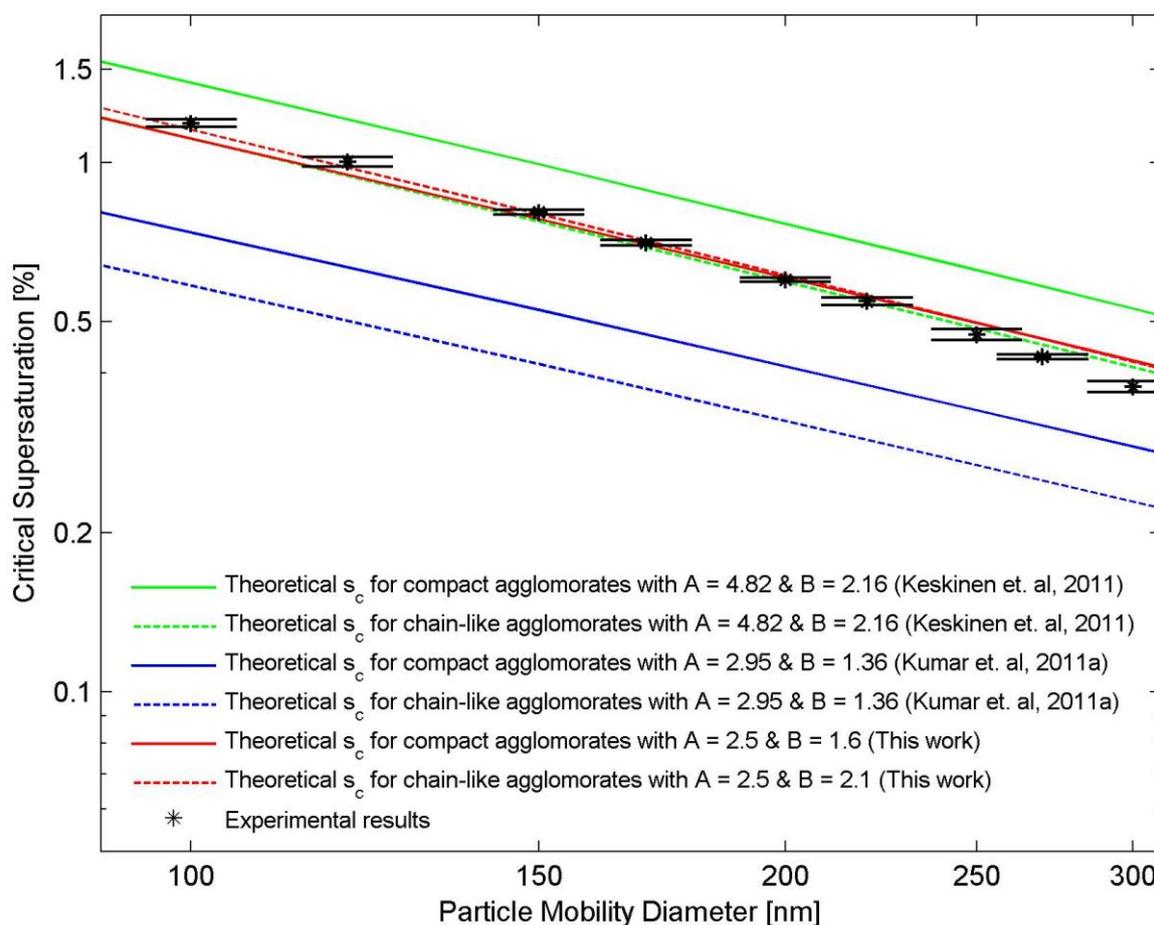


Fig. R1: Critical supersaturations against the critical mobility diameter of pure silica particles with different FHH adsorption isotherms and assuming either compact but porous agglomerates (solid lines) or chain-like agglomerates (dashed lines).

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

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

Given these overall results on the sensitivity to the shape assumption, we will revise the manuscript by applying the “compact agglomerate” assumption (i.e. $d_b = d_{ve} = d_{se}$) in all the theoretical calculations (in particular Eqs. 12-13) and the corresponding figures of the revised manuscript.

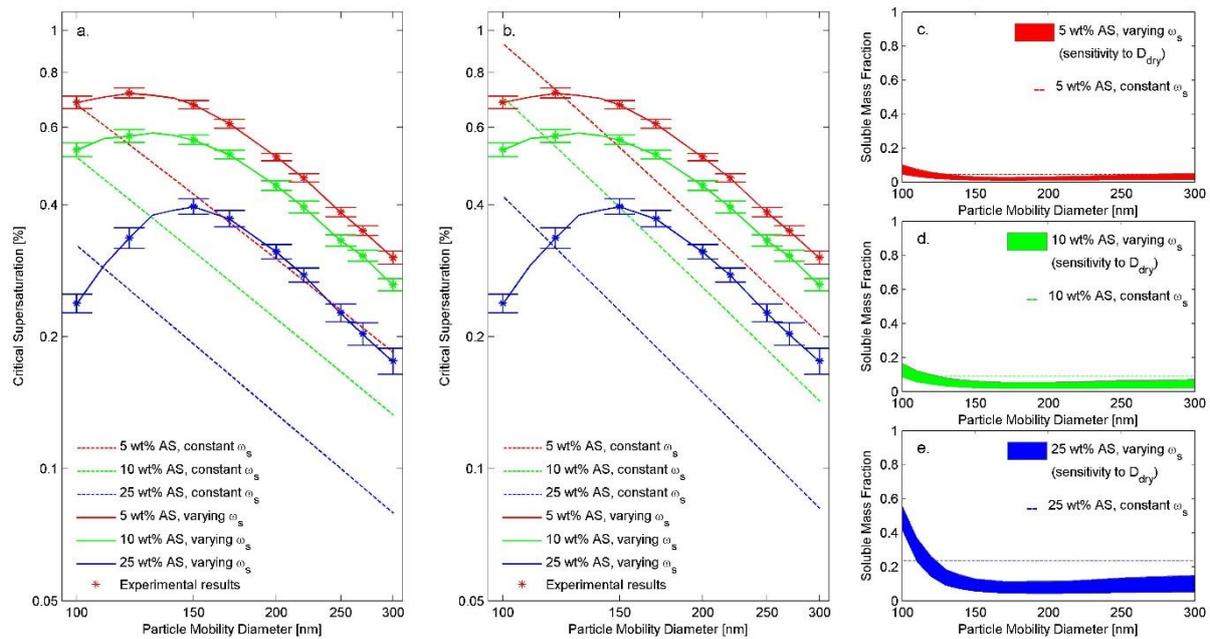


Fig. R2: Experimental and theoretical critical supersaturations for mixed silica + $(\text{NH}_4)_2\text{SO}_4$ (AS) particles vs. particle mobility diameters using different assumptions of particle shape and porosity. a) Critical supersaturations calculated assuming “compact agglomerates” for constant 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.

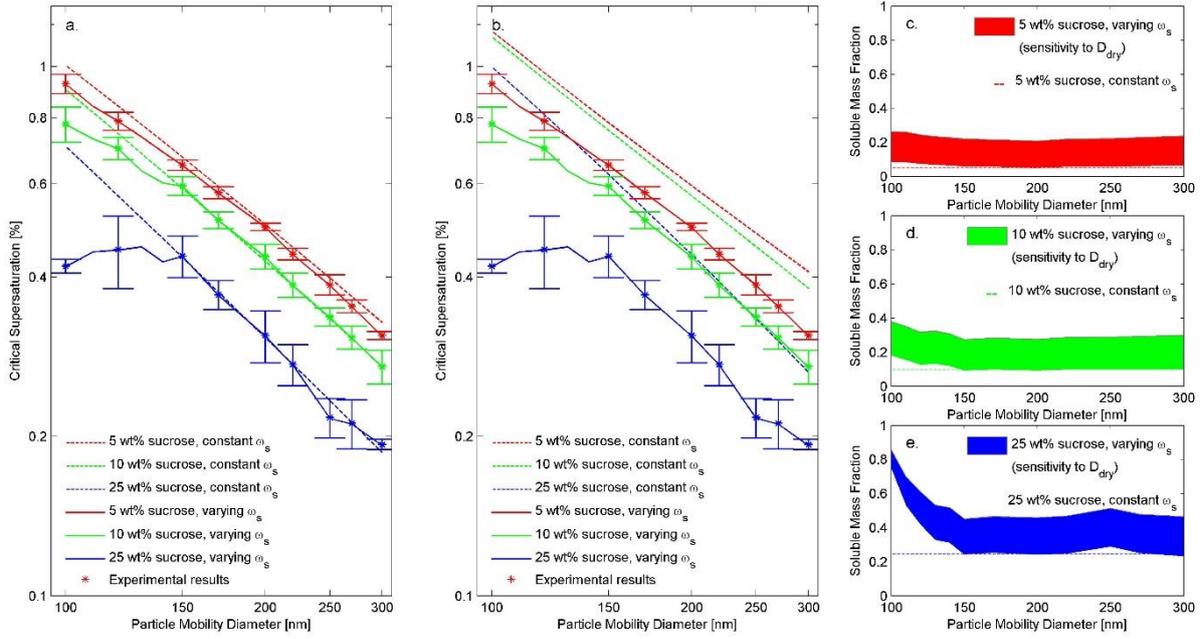


Fig. R3: Experimental and theoretical critical supersaturations for mixed silica + sucrose particles vs. particle mobility diameters using different assumptions of particle shape and porosity. a) Critical supersaturations calculated assuming “compact agglomerates” for constant and varying ω_s . b) Critical 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.

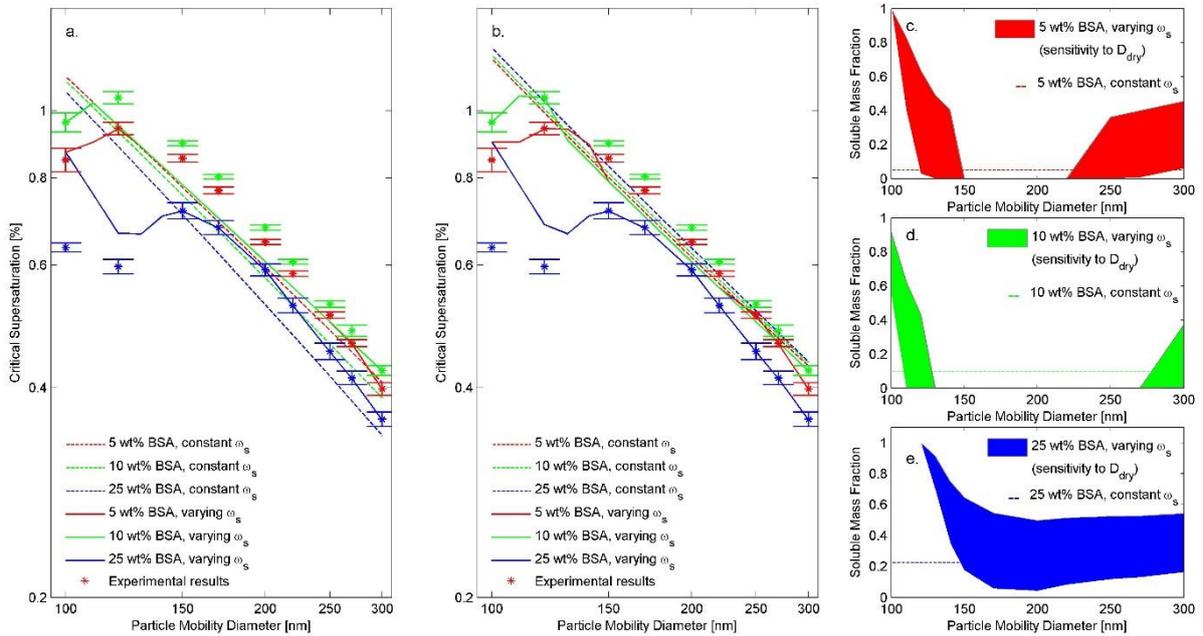


Fig. R4: Experimental and theoretical critical supersaturations for mixed silica + BSA particles vs. particle mobility diameters using different assumptions of particle shape and porosity. a) Critical supersaturations calculated assuming “compact agglomerates” for constant and varying ω_s . b) Critical 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.

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 will rather use 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 (2011a) 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 will revise 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 will modify 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 $> 10 \text{ M}\Omega\text{-cm}$ and TOC concentration $< 5\text{ppb}$ was used in our experiments. We will add 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 will be 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 will replace $\varepsilon = 1 - \varepsilon$ 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 will replace ω_{sS} with ω_s and ε_{sS} with ε_s in the revised manuscript.