**Atmospheric
Chemistry
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Discussions**

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Interactive comment on "Amorphous and crystalline aerosol particles interacting with water vapor – Part 1: Microstructure, phase transitions, hygroscopic growth and kinetic limitations" *by* E. Mikhailov et al.

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Response to Referee #1

We thank anonymous Referee #1 for the review of our manuscript. The constructive suggestions for improvement are very welcome and will be largely implemented upon revision. Detailed responses to the individual comments are given below.

Referee Comment 1:

This is an interesting paper, condensing several emerging threads in aerosol water

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interactions into a single publication. It contains detailed discussion on the HTDMA technique, various phase transitions including amorphous phases and gels, and water activity modeling. The paper is thoroughly researched and generally well written. However, the manuscript is repetitive in parts and much of the discussion should be presented in a significantly more concise form. The proposed particle microstructure and phase transitions are plausible and thought provoking. Nevertheless, by the authors own admission, it is difficult to unambiguously distinguish between restructuring and solid to semi-solid phase transitions just by measuring changes in dry particle size. In the manuscript only three compounds are examined, all of which have been reported on before in the peer-reviewed literature. This is mainly justified due to improvements in measurement accuracy and the inclusion of evaporation data and heterogeneity measures. In the final section of the manuscript, the growth factor data are modeled using a variety of currently used techniques, providing interesting insights into the non-ideal behavior of aqueous ammonium sulfate, oxalic acid, and levoglucosan solutions. The paper meets the standards of ACP and I recommend it for publication after addressing my concerns outlined below.

Response:

Thanks for the positive overall evaluation of our work. With regard to reporting data only for three substances that have already been investigated in earlier studies, we would like to point out that our study and manuscript have two main goals: (1) introduce a conceptual framework for the interaction of solid as well as semi-solid and crystalline as well as amorphous aerosol particles with water vapor; and (2) exemplify how this framework helps to consistently analyze and interpret experimental observations from our own as well as earlier studies.

We will clarify these aspects upon revision. We intend to adjust the title, restructure the manuscript, and separate the general conceptual framework (new Sect. 2 after introduction) from the presentation and discussion of our experimental results (new Sect. 4 after experimental methods) and of our model calculations (new Appendix

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B after Köhler model description). We hope and expect that these modifications will improve the conciseness and readability of the manuscript without compromising the completeness.

Referee Comment 2:

1.Much of this work hinges on the claim that the precision of the growth factor measurement "precision is generally better than 0.2 nm" and "the uncertainty in gb less than 0.4%" (I presume this is the accuracy). This precision enables detection of monolayer coverage on 100 nm particles. Although the authors give a fairly thorough instrument description I find this performance difficult to believe. As the authors state themselves, the humidity is expected to change the flows, leading to diameter uncertainties of up to 1 nm, more than a factor 2 larger than the 0.4%. Did the authors test this effect with PSL?

Response:

We have used PSL particles to check the absolute sizing accuracy of the applied SMPS system (DMA2) with the following results: For PSL particles with diameters of (100+/-4.8) nm and (83+/-2.7) nm as specified by the manufacturer (Postnova Analytics GMBH), the SMPS yielded diameters of (103.8+/-0.6) nm and (81.5+/-0.5) nm, respectively (arithmetic mean and standard deviation of 10 repeated measurements). The relatively high uncertainties of the measurement results for the PSL standard particles are due to bad counting statistics (low particle number concentrations required to obtain single particles upon nebulization).

We have not used PSL particles to check RH effects on particle sizing, because PSL particles are usually stabilized by charged sulfate and hydroxyl groups on the surface. In spite of the hydrophobicity of the particle bulk material, the surface functional groups are likely to induce water adsorption. Thus it would be difficult to unambiguously interpret observations of small changes of PSL particle diameters with RH. Moreover, the low aerosol particle number concentrations that are usually achieved with PSL stan-

dard solutions (low concentration required to obtain single particles upon nebulization) lead to bad counting statistics and relatively large uncertainties in particle diameter (∼0.5 nm standard deviation for 10 repeated measurements - see above).

Please note also the following:

1) None of the main conclusions of our study really depends on the high measurement precision of our experiments. Nevertheless, the high precision has been achieved as specified in the text and illustrated in Fig. 2a of our manuscript.

2) Even if the measurement precision were not better than ∼1% or ∼1 nm (for which we have no indication except at high RH in the h&d experiments), this would not affect the results and conclusions of our study. The only aspect for which the very high precision is really important is the calculation of equivalent numbers of monomolecular layers of water adsorbed on non-deliquesced particles (N_ML). The low scatter of the calculated N_ML values and their consistency with earlier studies (Sect. 3.2.2, Romakkaniemi et al., 2001; Biskos et al., 2006) clearly indicated that the measurement precision was as high as specified in our manuscript.

3) As discussed in our manuscript (end of Sect. 2.2), measurement uncertainties of the order of ∼1 nm may arise from kinetic limitations in HTDMA mode 3 (hydration&dehydration). The possibility of such measurement uncertainties at high RH are fully taken into account in our argumentation and conclusions of the results and discussion section.

4) Last but not least we would like to point out that the very good agreement of our measurements with Köhler model calculations using the AIM reference model reconfirms the high precision of the reported measurements (Sect. 5.3.1: mean relative deviation <1%).

Referee Comment 3:

The discussion on the flow control regulation is omitted and it is not clear that whether

this performance holds for all humidities. Further, the method uses SMPS scans to obtain the humidified size distribution. The standard TSI inversion software is not designed to accurately invert quasi-monodispere distribution that has been preselected by a DMA upstream; many effects specific to tandem DMA inversion (Gysel et al., 2009; Rader and McMurry, 1986) are not included. These effects may be relatively small, but given that the quoted accuracy is at the limit of what Rader and McMurry suggest that can be resolved theoretically, accurate inversion of the data is required. To rectify this the authors need to: (a) state the flow setup and quote the precision and accuracy of the flows as a function of RH, (b) include proper TDMA inversion of the data, (c) discuss if and how the RH effect on flow and particle size was corrected for in the data, (d) discuss if and how the drift in size was accounted for. Sheath and aerosol flow rates should be reported.

Response:

(a) In the DMA2 (TSI Model3071) the standard mass flow meters for the sheath and excess line (TSI Model 2011B) were calibrated using a film flow meter (Gilian Gilibrator 2, standard flow cell, accuracy 0.2%). At the beginning, middle and end of every experiment the film calibrator was used to check the sheath and aerosol flow rates, which were generally very stable (variations <0.5%). This information will be added in the revised manuscript.

(b) As specified in our manuscript we have used the standard TSI inversion software (TSI AIM 4.3 software) to convert raw measurement data into particle size distributions which were then fitted by lognormal distribution functions to obtain modal diameters and hygroscopic growth factors, respectively. This corresponds to the second approach discussed by Gysel et al. (2009: "inversion of DMA2 only"), for which Gysel et al. show and state that it is "correct" and "fulfills all specifications". In fact, Gysel et al. (2009) also state that correct growth factors could be determined even without data inversion for "samples exhibiting monomodal growth" as is the case in our study. Accordingly, also Mifflin et al. (2009) stated: "For the inversion algorithm (TSI) used to obtain par-

ticle number-diameter distributions, no corrections were made in the data analysis for the tandem setup (e.g., TDMAFIT) because the corrections, though significant for the shape or the height of a distribution, were inconsequential for the mode of the distribution ...". With regard to Rader and McMurry (1986), we would like to point out that they had indeed also achieved (and not just theoretically suggested) experimental precisions <= 0.2% (see Table 3 and related text in their paper), and they explicitly suggested that the achievable measurement precision corresponds "to the characteristic thickness of a monolayer". Last but not least, the applicability of our approach is confirmed by the good agreement achieved for ammonium sulfate calibration aerosol as pointed out above and detailed in our manuscript. We are not aware of any other studies (using advanced algorithms or not) that would have achieved and reported better agreement between measurement and reference model results for ammonium sulfate as well as sodium chloride calibration aerosols (Mikhailov et al., 2004 and additional unpublished results for NaCl, deviation < 1%).

(c) As specified above, there was no need to correct for RH effects on the flow rates, which were controlled with high precision. Potential effects of RH changes on particle mobility sizing with the SMPS, i.e., effects of changes in mean free path and viscosity on electrical mobility, were estimated using the empirical formulas reported by Weingartner et al. (Atmos. Environ., 31, 15, 2311-2325, 1997). Overall these effects should influence the observed growth factors by less than ∼0.3%. As this is within the specified uncertainties, we have chosen not to correct the measurement data. This information will be added in the revised manuscript.

(d) As specified and demonstrated in our manuscript (Sect. 2.3, Fig. 2), the diameter drift in our experiments was generally less than 0.2% and thus within the reported uncertainty of 0.4%. Db.i was checked at the beginning, middle and end of every experiment. The measurement data were not corrected for drifts of Db.i, but the experiment was discarded and repeated if the drift exceeded 0.2%. This information will be added in the manuscript. Sheath and aerosol flow rates are already specified in our

manuscript (p. 7431, l. 17).

Referee Comment 4:

2. I object to the redefinition of deliquescence. By definition, the deliquescence relative humidity (DRH) is the humidity where a particle absorbs water and forms a saturated solution (Seinfeld and Pandis, 1998). With that DRH is solidly grounded in thermodynamic equilibrium theory. In contrast, efflorescence requires a supersaturation with respect to the solid and thus is not an equilibrium concept. This should be clarified in the manuscript where DRH and ERH are both denoted as equilibrium concepts. Extending DRH to non-equilibrium cases as proposed in this paper will certainly lead to confusion. As stated in the manuscript particles composed of at least three components (2 solutes + water) can undergo deliquescence where the salt forms a ternary saturated solution. Sometimes this has been referred to gradual dissolution of the second solid in the literature. These well defined cases are easily confused with gradual and/or partial deliquescence proposed here, where gradual refers to a kinetic limitation, and partial deliquescence to a special phase transition. I strongly urge the authors to consider a new term for this phenomenon, e.g. the liquefaction as used sometimes in the manuscript.

Response:

We understand and respect but do not share the referee's opinion that the term deliquescence should be restricted to crystalline phases and equilibrium transitions. The more general definition that we propose is consistent with but goes beyond the definition advocated by Referee #1 and used by Seinfeld and Pandis (1998) who did not deal with amorphous/semi-solid substances.

As explained in our manuscript, the term deliquescence has not originated from and is not restricted to atmospheric science, where up to now it had generally been associated with crystalline substances. The references quoted in our manuscript and most other references that can be found in dictionaries, glossaries, and throughout the

internet define deliquescence essentially as proposed in our manuscript: liquefaction of a solid upon exposure to humid air/gas (humidification). We agree that one could possibly also use the simple terms liquefaction (or liquescence) and solidification as abbreviations for the full terms specified in our manuscript (liquefaction upon humidification/hydration vs. solidification upon drying/dehydration). However, we think that these short terms alone would not be suitable, because they are too general. For example, the term liquefaction (or liquescence) as such would include also other forms of "becoming liquid" (melting, glass transition, dissolution upon mixing with a liquid, ...).

If we did not use the term deliquescence in its general meaning, we would have to define not only one but two additional new terms: one term like "liquefaction (or liquescence) upon humidification (from the gas phase)" for the general phenomenon that (semi-)solid substances(both crystalline and amorphous) can become liquid (liquesce) upon exposure to humid air/gas (for which most general/scientific dictionaries use the term deliquescence), and one term like "amorphous liquefaction upon humidification (from the gas phase)" for non-crystalline (semi-)solid substances that become liquid upon exposure to humid air/gas.

We think that it is more efficient and beneficial for scientific communication across the atmospheric sciences and beyond to use the (already existing and widespread) general definition of deliquescence as an umbrella term. Please note that earlier studies have already used the term deliquescence in a way that goes beyond classical equilibrium phase transitions and deliquescence points - see discussions of pre-deliquescence, non-prompt, nucleated, and other pathways of deliquescence (e.g., Cantrell, W., Mc-Crory, C., and Ewing, G. E.: Nucleated deliquescence of salt, J. Chem. Phys. 116, 2116, doi:10.1063/1.1429924, 2002; Biskos et al., 2006; Zardini et al., 2008; McGraw, R. and Lewis, E. R.: Deliquescence and efflorescence of small particles, J. Chem. Phys., 131, 194705, 2009; and references therein). For clarification we intend to include the preceding statement and references in the revised manuscript.

When dealing with crystalline substances – as assumed in most earlier atmospheric

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studies – deliquescence can be regarded as a classical equilibrium phase transition with a (more or less) well-defined deliquescence point. When dealing with amorphous solids (glasses) or other (semi-)solid substances (gels, rubbers, etc.), deliquescence can be regarded as a non-equilibrium phase transition like the glass transition. Studies explicitly discriminating different forms of deliquescence can simply add appropriate adjectives or nouns: crystal(line) deliquescence, amorphous deliquescence, glass(y) deliquescence, rubber(y) deliquescence, gel deliquescence, etc.

This may appear complicated at first sight, but an umbrella term "liquefaction (or liquescence) upon humidification (from the gas phase)" with the specialized sub-terms deliquescence (of crystals only), "glass(y) liquefaction/liquescence upon humidification (from the gas phase)", "amorphous liquefaction/liquescence upon humidification (from the gas phase)", "rubber(y) liquefaction/liquescence upon humidification (from the gas phase)", "gel liquefaction/liquescence upon humidification (from the gas phase)" would be even more complicated.

Thus we maintain the proposition expressed in our discussion paper, and we encourage the scientific community to consider the above arguments and to choose and use the most suitable definition for further scientific communication. For clarification, we intend to add some of the above arguments in the revised manuscript (second last paragraph: When dealing with crystalline substances . . .).

Referee Comment 5:

3. With respect to liquefaction the authors should more thoroughly discuss the proposed mechanisms. The possibility of non-equilibrium in HTDMA measurements for organics has been discussed by Sjogren et al. (2007) and some discussion about diffusion kinetics in growing droplets by Taraniak et al. (2007). A detailed theoretical equilibrium understanding of nanoparticle deliquescence was developed by Russell and Ming (2002), who note that many soluble species in air above 45% are wetted with multiple layers of water molecules and provide a sound description of the existence of

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the water layers based on free energy arguments. Void spaces were experimentally discussed by Weis and Ewing (1999). These manuscripts should be acknowledged and those previous findings discussed in comparison to the findings presented here.

Response:

We will include the suggested references in the revised manuscript. Note, however, that the model of Russell and Ming (2002) deviated substantially from experimental results. Accordingly they stated: "... but data taken in the deliquescence region cannot be explained". A detailed discussion of the various mechanisms and molecular processes that may be involved in different systems and the kinetic or thermodynamic models that may be applicable would certainly be interesting but goes beyond the scope of our paper.

Referee Comment 6:

4. It is well known that pure particles cannot be generated from atomization and that impurities in the water can affect the CCN measurements of slightly soluble substances (Bilde and Svenningsson, 2004). Impurities lead to water uptake at RH lower than the DRH of the compound studied, and lowers the DRH of the particle. I would expect impurities to play at least some role in the changes reported here.

Response:

As describe in our manuscript, we have checked the properties of the crystalline starting materials by measurements of relative humidity over saturated aqueous samples. The obtained values were in a good agreement with the DRH values reported in earlier studies (Table2) and indicate no significant influence of impurities on the properties of the investigated substances. Thus we see no way how impurities could plausibly explain the observed strong, gradual and reversible water uptake at much lower relative humidity than the DRH of the crystalline starting materials. We also cannot see how impurities could plausibly explain the observed restructuring and broadening effects,

and we are not aware of any studies indicating such effects.

Bilde and Svenningson (2004) have shown that small impurities of highly hygroscopic materials can enhance the CCN activity of largely insoluble particles, which is consistent with Köhler theory. However, it is not clear (and Referee #1 provides no conclusive arguments or references) how impurities should induce the phenomena observed in our HTDMA study. Beyond that, many of our conclusions about the occurrence and properties of amorphous organic substances are also based evidence from numerous earlier studies (food, pharmaceutical and materials science). Nevertheless, we agree that impurities may in general have an influence on the formation and properties of crystalline or amorphous phases. Further investigations and discussions of this topic, however, go beyond the scope of our study.

Referee Comment 7:

5. Can the authors really distinguish gels, rubbers, and amorphous states? Clearly HTDMA data alone only detects changes in size. Phase changes in the HTDMA cannot be inferred without knowing what "dry" solid was generated, and what other stable (semi-solid) phases exist. Therefore the argument should always be forward, i.e. the HTDMA observations are consistent with the formation of phase X, but never be backwards, i.e. we infer a solid-solid phase transition from the HTDMA for unknown substances. This point should be made clearly in the paper. Further, the initial phase state is rarely known and not verified here. Again this point needs to made and caveats of the very inferential nature of the inquiry added to paper. The restructuring suggests that it is likely amorphous and this results in uncertainty in the thermodynamic quantities derived from growth factor data. However, this fact is well known has been discussed in the literature (Mikhailov et al., 2004; Mochida and Kawamura, 2004).

Response:

We appreciate and share the referee's general concern that careful wording should be used in scientific writing and argumentation. We have done our best to formulate the

manuscript in a way that clearly discriminates between what has been experimentally observed, how the experimental findings can be plausibly explained/interpreted, and what the specified findings and interpretation further indicate in view of the scientific literature and general concepts outlined at the beginning of the manuscript.

Please note that we have very clearly indicated interpretative statements by phrases like "can be explained by", "most plausibly explains", "appear to be the most plausible explanation", "appear to have been", "apparently", etc. The need for carefully differentiated argumentation is the main reason why we do not consider it a good idea to convolute and condense the discussion of the different investigated systems. Instead, we consider it necessary to very clearly and explicitly demonstrate and argue for each of the investigated systems separately what we observed and how we interpret the observations.

Unfortunately, Referee #1 did not indicate where exactly he/she considered our formulations to be inappropriate. Maybe it was in the summary and conclusions section, where we will add some caveats and formulations emphasizing the inferential nature of some of our conclusions.

With regard to the distinction of gels, rubbers and (other) amorphous states (like glasses or ultraviscous liquids) we have stated very clearly in our discussion paper that further investigations will be required to unambiguously discriminate different semi-solid phases and their relevance. For example, we stated on p. 7363 in lines 4 and 14: "...suggest that the formation and transformation of gel-like structures or nonuniform concentration gradients (e.g., semi-solid shells) played a role in the kinetically limited deliquescence transition." "Further investigations will be required to explore under which conditions glassy, rubbery or gel-like structures may be important ..."

Nevertheless, it appears difficult to explain the reported observations for oxalic acid particles without assuming that they had gel-like porous structures. We have tried but could not find plausible alternative explanations. As far as we can see, the experimental

findings, analyses, interpretations and conclusions of our study go far beyond what has been presented by Mikhailov et al. (2004) and Mochida and Kawamura (2004).

Referee Comment 8:

6. Much of the discussion could be presented more concisely. Discussion for the three compounds can be synthesized into a single paragraph, thereby eliminating repetitiveness; this should be done for both the phase transition part and hygroscopicity modeling part. Several parts of the manuscript feel more like a review article (e.g. the general discussion about the different solid phase states, or the use AIM in thermodynamic modeling and CCN calibration). These parts should be condensed further since they don't apply directly to the findings here. In general the length of the manuscript is distracting and many of the important ideas presented here will be missed by a broad audience if the paper remains this verbose.

Response:

As mentioned above, we do not consider it a good idea to convolute and condense the discussion of the different investigated systems. Instead, we consider it necessary to explain for each of the investigated systems very clearly and explicitly what we observed and how we interpret the observations. We do not think that any parts of our manuscript would not be relevant for the conceptual framework outlined, the experimental findings reported, and the conclusions presented in our manuscript.

In particular we consider the synthesis of information about different (semi-)solid phase states that may be relevant for (atmospheric) aerosol particles as a key element of our manuscript. It is the basis of the proposed conceptual framework, and we are not aware of any scientific publications where the interested reader could find a comparable synthesis. With regard to the AIM we consider it relevant to explain why we regard and use it as an accurate reference model, because we know that interested members of the scientific community have/had not yet recognized that it can indeed be regarded and used as an accurate reference for both CCN and HTDMA experiments. To our

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knowledge, earlier HTDMA studies had not yet demonstrated similarly good agreement between experimental data and AIM-based Köhler model calculations.

Following the referee's recommendation to focus on the key messages and condense the main manuscript, we will move the entire Köhler model section including Figs. 6 and 7 into the appendix and we will shorten the discussion of AIM-based reference models. As indicated above, we will also separate the general conceptual framework (Sect. 2 after introduction) from the presentation and discussion of our experimental results (Sect. 4 after experimental methods) and of our model calculations (Appendix B after Köhler model description). We hope that this will improve the readability and usefulness of our paper for readers who may not be interested in all aspects of our study.

Note, however, that we consider it good scientific practice to present all relevant data, aspects, arguments and steps of scientific analyses. We are aware that short papers presenting little detail tend to attract less criticism, but we prefer presenting our work in a comprehensive format on which interested colleagues can build without guessing. Readers who are not interested in the details but just want to know the quintessence and main messages of a study can simply focus on the abstract and conclusions section.

Referee Comment 9:

7. The authors seem to be surprised that FH theory applies for low molecular weight compounds. It can be shown that for f = 1 and chi = 0 Raoult's law is obtained. Since chi represents the enthalpy of mixing and for small f the residual term accurately captures the entropy of mixing, FH is a fully adequate description of the free energy of mixing, and hence water activity. With constant chi, FH theory is simply another single parameter model of hygroscopic growth.

Response:

We agree, but we did not consider it self-evident that the FH model was better suited to describe the hygroscopic growth of LG than the IS and UNIFAC models. Following up on the referees comment, we intend to clarify the statement about the suitability of the FH model in the revised manuscript.

Referee Comment 10:

What it demonstrates, however, is that equation A19 is questionable (if not outright invalid) when applied to larger molecules and thus should not be used, or suggest to be used, in estimation of the hygroscopicity parameter from solute property data when osmotic coefficient data must be guessed. The problem of attributing kappa to molecular weight and density of the solute is fact that equation A19 does not accurately capture the effect of molecular size on the entropy of mixing. Thus equation A19 is only valid for molecules with f near unity (in ionic compounds achieved through dissociation). For f « 1, the van't Hoff factor or osmotic coefficient will then compensate for the neglected entropy effect leading to unrealistic van't Hoff factors of 100 for macromolecules as shown by the lead author in one of his previous publications.

Response:

We agree that the usefulness of eq. A19 is limited in the sense that for large molecules the van't Hoff factor loses the physical meaning that it has for solutions of small ions. However, we do not agree that the equation would be "outright invalid", because it is still consistent with the basic definitions of the involved quantities and parameters. Note that already for simple ionic compounds the van't Hoff factor is essentially not more than an empirical parameter that allows to relate water activity to the concentration of the solute and is more or less close to the number of ions formed by dissociation of the solute in solution. For large molecules such as protein macromolecules, Mikhailov et al. (2004) have indeed shown that and how the van't Hoff factor or the product of stoichiometric dissociation number and corresponding osmotic coefficient, respectively, loose their meaning as an "effective dissociation number" and exhibit a strong concen-

tration dependence. However, Mikhailov et al. (2004) have also shown that and how the osmotic coefficient and thus the van't Hoff factor can be calculated/approximated from osmotic pressure equations and solute volume fractions.

Referee Comment 11:

The geometric standard deviation of the humidified size distribution is a useful quantity that adds valuable information about the phase transitions and/or heterogeneity of the input distribution. The authors should overlay the predicted sigma_g from DMA theory to show where broadening occurred.

Response: We appreciate this suggestion, but it goes beyond the scope of our paper where we just use the measurement-derived geometric standard deviation as a relative indicator for processes that induce a broadening of the size distribution.

Referee Comment 12:

The polynomial's shown in Figure 5 lead to a awkward curves (i.e. Figure 5 d). Since they only serve to guide the eye it might be better to use splines to obtain a smooth curve. The reference Raatiken and Laaksonen should be Raatikainen and Laaksonen

Response:

We will implement the suggested improvements in the revised manuscript.

Referee Comment 13:

The value k = 0.21 given in Petters and Kreidenweis (2007) is for levoglucosan derived from CCN activation. The proper value to compare to is 0.17 which is based on growth factor data.

Response:

We understand the difference and had intentionally reported both values. As explained in our manuscript, we think that the low kappa value calculated by Petters and Krei-

denweis on the basis of earlier H-TDMA experiments (0.17) is likely due to experimental artefacts (incomplete particle drying) rather than to concentration dependencies that normally cause differences between kappa values (and equivalent parameters) determined in H-TDMA and CCN measurements. We will clarify this in the revised manuscript.

Referee Comment 14:

Do the concepts apply for mixed organic/inorganic particles. Is it really necessary to separate the mixed particles into a second paper? There is only data for three systems, and the mixed particles could easily be added here.

Response:

As already mentioned in the discussion paper, the presented concepts do apply also for mixed particles as will be shown in a companion paper. We do consider it necessary to report the mixed particle results in a separate paper. The published discussion paper is already fairly long, and the companion paper will not be much shorter, because it will address additional aspects (mixing effects and interactions between different substances) that go beyond the fundamental differences of amorphous and crystalline particles as outlined and exemplified in this manuscript. As mentioned above, we consider it necessary and good scientific practice to present all relevant data, aspects, arguments and steps of our analyses, and we prefer presenting our work in a format on which interested colleagues can build without guessing.

Referee Comment 14:

The conclusions 'form most organics' is overstated since only OA and LG data were studied here.

Response:

We disagree. As explained in our manuscript and supported by a large number of references, there is ample evidence that indeed most organics tend to form amorphous

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solids upon spray drying. Based on the available information it is indeed likely that very few if any organic compounds would form crystals upon spray draying. We consider it normal and important that scientific studies like ours and others can and shall build on the available body of scientific literature and knowledge and not only on newly recorded and reported experimental data.

Referee Comment 15:

Liu et al. (2008) did a detailed study of the hygroscopic properties of Ca(NO3)2 that is missing from his discussion.

Response:

Thanks, we will include this reference in the revised manuscript.

Referee's References:

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 7333, 2009.