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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.

Anonymous Referee #1

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

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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.

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 g_b 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? 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 pre-selected 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.

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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.

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 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.

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

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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.

5. Can the authors really distinguish gels, rubbers, and amorphous states? Clearly HT-DMA 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 be 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).

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.

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 χ 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 χ , FH theory is simply another sin-

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gle parameter model of hygroscopic growth. 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 $f \ll 1$, 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.

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.

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

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.

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.

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

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studied here.

Liu et al. (2008) did a detailed study of the hygroscopic properties of $\text{Ca}(\text{NO}_3)_2$ that is missing from his discussion.

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