

## Response to Anonymous Referee #1

The referee's comments are in italics, our responses in plain font.

*This paper presents a description of a HHTDMA and related method developed for investigating the hygroscopicity of aerosols in RH range of 2-99.6% with the uncertainty of growth factors within 0.9%, which will help explore the interaction between water and aerosols at RH close to 100%. By combining the restructuring modes with hydration/dehydration modes, the GFs can be measured in high precision after the microstructural rearrangement effect is considered. The manuscript is well written and presents a valuable contribution in the field of aerosol measurement techniques. I recommend this manuscript to be published after the following issues to be addressed and modified.*

We thank the Referee #1 for the suggestions for improvement that were taken into account upon manuscript revision. Responses to individual comments are given below.

### *Specific comments:*

*Section 2.1: The manuscript gives a general description about the design and the components in constructing the HHTDMA. However, temperature and humidity control should be critical issues in operation, for example, maybe a PID control program was used with the input of RH4 and RH5 probe to control the RH in DMA2 precisely.*

The temperature and RH control is discussed in Sect. 2.1 and Sect 2.4, respectively. PID control program was not used. The temperature **gradient**, i.e. the temperature profile along the DMA2 column ( $dT/dL$ ) was not directly measured. The temperature difference between sheath and excess flow was used to estimate temperature variation inside DMA2 as indicated in Sect. 2.1.

### *How did the GORE-TEX membrane work?*

The following clarifying text has been added in Sect. 2.3 to explain how Gore-Tex membrane was used:

The humidity of the aerosol flow (RH3) and sheath air (RH4) in DMA2, is controlled by mixing water saturated and dry air flows in a ratio produced the desired RH. Saturated air is obtained by passing dry air through a Gore-Tex membrane tube submerged inside a temperature controlled water bath ( $27.0 \pm 0.1$  °C). Two separate 6 mm (ID) Gore-Tex tubes, 0.5-m and 2-m long are used for aerosol and sheath flows conditioning, respectively (Humidifier, Fig. 1). For the H1 Nafion exchanger the humid air is prepared by bubbling air directly through water and then mixing with dry air to the required humidity (not shown in Fig.1).

### *How to adjust the rotation speed of the fans in the DMA2 box?*

The fan speed can be changed by varying the applied voltage (manually), but this was not necessary. In Supp. 2.1 we have demonstrated a simple way to compensate for the temperature difference between sheath and excess flows, if it needed.

The text in Suppl. 2.1 was modified as following:

The test measurements showed that the temperature difference between the sheath and excess flows can be changed within  $\pm 0.3$  °C by adjusting the rotation speed of the fans. The speed of each fan is affected by applied AC voltage.

*Page 13, Line 358-360: This sentence is obscure and should be rewritten.*

The sentence is updated:

The FHH (Frenkel, Halsey and Hii) model is the frequently used to relate surface coverage to a water activity:

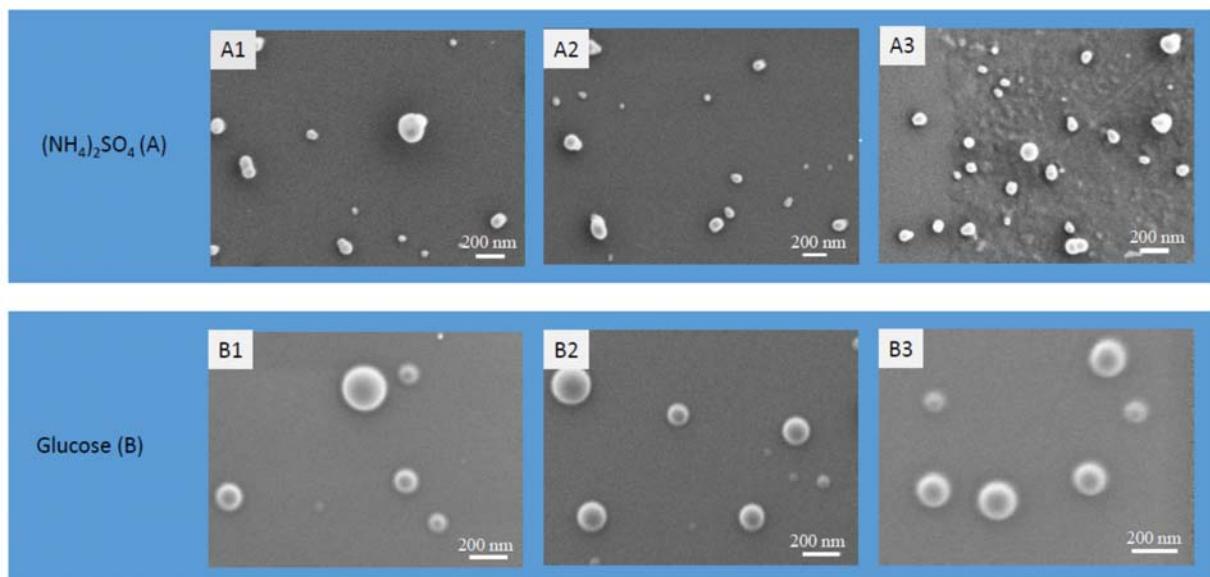
$$a_w = \exp(-A_{FHH}/\Theta^{B_{FHH}}), \quad (28)$$

where  $A_{FHH}$  and  $B_{FHH}$  are empirical fit parameters that describe the intermolecular interactions governing the adsorption potential.  $A_{FHH}$  characterizes interactions between the surface and first adsorbed water layer as well as interactions between adjacent molecules.  $B_{FHH}$  describes the interactions between the surface and subsequent adsorbate layers.

*Page 16, Line 470-480: I recommend providing more proofs (e.g. SEM images of particles) or reference(s) to support this claim.*

The conclusion about the difference in the porous structure of ammonium sulfate and glucose particles is based on the results of HHTDMA measurements in the h&d mode. To our knowledge, there are no direct methods for measuring the pore network of 100 nm particles. SEM is a useful technique for extracting two-dimensional (2D) images of the microstructures but does not provide the third spatial component of the sample, which is important to find interconnected regions and pore volumes, shapes and sizes.

We have added the SEM images of initial ammonium sulfate and glucose aerosol particles (Fig. 5) in order to strengthen the argument in favor of the discussed aerosol particles morphology and the calculated values of particle shape ( $\chi$ ,  $\beta$ ) and porosity ( $\delta$ ,  $f$ ) presented in Table 1.



**Fig. 5** SEM images of initial ammonium sulfate (A) and glucose (B) aerosol particles. The samples were investigated with a high-resolution SEM (ZEISS Merlin). Operation conditions: 0.4 kV accelerating voltage, 1.5 kV ESB grid voltage, 1.8 mm working distance. Particle samples were collected directly onto a 3mm TEM copper 300 mesh grids, coated with a 30–60 nm thick Formvar film.

Response to Anonymous Referee #2.

The referee's comments are in italics, our responses in plain font.

*Mikhailov et al. present an instrument characterization of a newly constructed high humidity tandem DMA instrument. The instrument shows improved capabilities compared to previously described setups. The manuscript is well written and I recommend it for publication in AMT.*

We thank the Referee #2 for these positive remarks. Responses to individual comments are given below.

*The authors might consider adding a section comparing the versatility and accuracy of the system with other techniques. Specifically the Leipzig based LACIS instrument and the filter-based mass-based hygroscopicity method used by the same author previously would be interesting to compare in this context.*

The following text has been added:

In addition to the HTDMA methods, other techniques have been used to determine the aerosol hygroscopicity at high RH (Tang et al., 2019). Two of these methods are the Leipzig Aerosol Cloud Interaction Simulator (LACIS; Stratmann et al., 2004) and the inverted streamwise-gradient cloud condensation nuclei counter (Ruehl et al. 2010), which could be operated at RH over the range of 85.8 – 99.1 % and 99. 4 – 99.9 %, respectively. Both methods have accurate humidity control, but the optical detectors used to determine the wet particle size distribution are subjected to limitations in accuracy resolution due to uncertainties in refractive index and the conversion from optical to physical diameter. This leads to uncertainty in the measured growth factors of ~ 4% (Wex et al., 2005).

Mikhailov et al. (2011) developed a filter-based differential hygroscopicity analyzer (FDHA), which was employed as an offline method to investigate hygroscopic properties of ambient aerosol particles (Mikhailov et al., 2013, 2015). An updated version of the instrument allows measuring the hygroscopic growth up to 99.6 % with accuracy of  $\pm 0.1$  % RH. The uncertainty in the determination of the mass growth factors was estimated to be ~1 % at 30 % RH and ~10% at 99 % RH. FDHA measures water mass absorbed by aerosol particles deposited on the filters. Due to mass conservation, this method is not influenced by the effects of capillary condensation and restructuring of porous and irregularly shaped particles that usually limit the applicability and precision of mobility diameter-based HTDMA and CCNC (Cloud Condensation Nuclei Counter) experiments. Since FDHA is katherometer-based technique, it takes on average of 2 days, to measure one aerosol sample, which is a drawback of this instrument.

*The authors state that activity coefficients can be determined from the data without the need to assume volume additivity by relying only on known (bulk) solution density. The authors should add that solution density is rarely known for metastable solutions and systems of interest to be studied with the HHTDMA.*

On line 338 the following text has been added:

For many atmospheric aerosols, the concentration dependence of the aqueous solution density is not well defined. At the same time, for a number of model systems of interest, the aerosol solution density was measured in both unsaturated and supersaturated solutions. In this case  $x_w$  can be obtained without assumption of volume additivity by iteratively solving Eq. (8) with other equation where  $\rho$  and concentration is given explicitly.

*The data should be made available in a FAIR aligned repository. Making data "available upon request to the author" is inconsistent with the AMT data policy ([https://www.atmospheric-measurement-techniques.net/about/data\\_policy.html](https://www.atmospheric-measurement-techniques.net/about/data_policy.html)).*

The data are available at <https://osf.io/87526/>

Response to Anonymous Referee #3.

The referee's comments are in italics, our responses in plain font.

*Mikhailov et al. present an instrument characterization of a newly constructed high humidity tandem DMA instrument. The instrument shows improved capabilities compared to previously described setups. The manuscript is well written and I recommend it for publication in AMT.*

We thank the Referee #3 for these positive remarks.

*Specific comments:*

*Page 2, line 52: replace “result” with “resulting”*

Corrected

*Page 2, line 63: replace “due” with “to”*

Corrected

*Page 2, line 67: add missing parenthesis after the citations*

Corrected

*Page 2, line 68: replace “effect” with “effects”*

Corrected

*Page 3, line 76: rephrase the sentence starting with “However, due to: : : : ”*

A new version is:

However, the resulting growth factor error at high humidity is significant since the relative humidity was obtained using a dew point sensor. (Further down in the text.) Thus, at RH = 97.7 % the precision quoted by authors in absolute units is  $\pm 1.2\%$  and particle growth factor uncertainty is 16.6 % ( $\pm 0.46$  at growth factor value of 2.79).

*Page 3, line 82: add “for” after “this instrument allows”*

Corrected

*Page 3, line 88: rephrase the sentence starting with “The averaged in the 80-99%...”*

The sentence was modified as following:

The resulting growth factor uncertainty associated with RH and instrumental errors is  $\sim 2\%$ , which is propagated in hygroscopicity and activity coefficients of  $\pm 20\%$ .

*Page 4, line 110: add “a” in front of “circulation thermostat”*

Corrected

*Page 4, line 111: add “are” before “operated at 26C..”*

Corrected

*Page 4, line 114 and following: I would suggest to use present tense and not past tense to describe the difference in e.g. PT100 sensors uncertainty.*

Corrected

*Page 5, line 145: replace “nebulize” by “nebulizing”*

Corrected

*Page 5, line 162: the units of 1 l/m should rather be 1 l/min*

Corrected

*Page 5, line 172: rephrase the whole sentence, very unclear*

The text was modified as following:

The humidity of the aerosol flow (RH3) and sheath air (RH4) in DMA2, is controlled by mixing water saturated and dry air flows in a ratio produced the desired RH. Saturated air is obtained by passing dry air through a Gore-Tex membrane tube submerged inside a temperature controlled water bath ( $27.0 \pm 0.1^\circ\text{C}$ ). Two separate 6 mm (ID) Gore-Tex tubes, 0.5-m and 2-m long are used for aerosol and sheath flows conditioning, respectively (Humidifier, Fig. 1). For the H1 Nafion

exchanger the humid air is prepared by bubbling air directly through water and then mixing with dry air to the required humidity (not shown in Fig.1).

*Page 7, line 214: wrong units for the error of the dry mobility diameter (should be nm)*

Corrected

*Please check carefully the whole manuscript for missing articles like “the” or “a”, singular and plurals and the use of past and present tense.*

Done.

# High humidity tandem differential mobility analyzer for accurate determination of aerosol hygroscopic growth, microstructure and activity coefficients over a wide range of relative humidity

5      Eugene F. Mikhailov<sup>1,2</sup> and Sergey S. Vlasenko<sup>2</sup>

<sup>1</sup>Multiphase Chemistry and Biogeochemistry Departments, Max Planck Institute for Chemistry, 55020 Mainz, Germany.

<sup>2</sup>St. Petersburg State University, 7/9 Universitetskaya nab, St. Petersburg, 199034, Russia

10     Correspondence to : E. F. Mikhailov (eugene.mikhailov@spbu.ru)

**Abstract.** Interactions with water are crucial for the properties, transformation and climate effects of atmospheric aerosols. Here we present high humidity tandem differential hygroscopicity analyzer (HHTDMA) and a new method to measure the hygroscopic growth of aerosol particles with *in-situ* restructuring to minimize the influence of particle shape. With this approach, growth factors can be measured with an uncertainty 0.3–0.9 % over a relative humidity (RH) range of 2–99.6 % and with an RH measurement accuracy better than 0.4 %.

The HHTDMA instrument can be used in hydration, dehydration and restructuring modes of operation. The restructuring mode allows to investigate the effects of drying conditions on the initial 20 microstructure of aerosol particles and specified the optimal parameters that provide their rearrangements into compact structures with near-spherical shape. These optimal parameters were then used in hygroscopic growth experiments by combining restructuring mode with conventional hydration or dehydration mode. The tandem of two modes allowed us to measure the particle growth factors with high precision as well as to determine the thickness of the water adsorption layer on the surface of 25 compact crystalline particles.

To verify HHTDMA instrument we compared the measured ammonium sulfate growth factors with these obtained from E-AIM-based Köhler model. Averaged over the range of 38–96 % RH, the mean relative deviations between measurement and model results is less than 0.5 %.

We demonstrate this precision by presenting data for glucose for which bulk thermodynamic 30 coefficients are available. The HHTDMA-derived activity coefficients of water and glucose were obtained for both dilute and supersaturated solutions and are in a good agreement with these reported in literature. Averaged deviation between the measured activity coefficients and these obtained by bulk method is less than 4 %. For dilute solution in water activity range of 0.98 - 0.99 the hygroscopicity

parameter of glucose and molal osmotic coefficient were obtained with uncertainty of 0.4 % and 2.5  
35 %, respectively.

## 1. Introduction

The hygroscopic properties of atmospheric aerosol particles are vital for a proper description of their  
40 direct and indirect effect on the radiative budget of the Earth's atmosphere (Hänel, 1976; Rader and  
McMurtry, 1986; Pöschl et al., 2005; McFiggans et al., 2006; Andreae and Rosenfeld, 2008;  
Swietlicki et al., 2008; Cheng et al., 2008; Zieger et al., 2013; Rastak et al., 2014; and references  
therein). The response of aerosol particles to changes in relative humidity (RH) can be obtained by  
45 determining the growth factor of aerosol particles under enhanced RH conditions. The latter is  
possible by means of a hygroscopicity tandem differential mobility analyzer (H-TDMA). The  
principles of TDMA experiments have been described four decades ago (Liu et al., 1978; Rader and  
McMurtry, 1986), and a wide range of applications and modifications of this technique have been  
50 reported since then (e.g. Brechtel and Kreidenweis, 2000; Weingartner et al., 2002; Mikhailov et al.,  
2004; Biskos et al., 2006; Johnson et al., 2008; Nilsson et al., 2009; Duplissy et al., 2009; Lopez-  
Yglesias et al., 2014). Due to technical limitation, most of the traditional HTDMA studies have been  
however conducted at RHs < 95 %. At higher humidity the HTDMA setup become less reliable due  
55 to small variations in temperature in the second differential mobility analyzer (DMA2) resulting in  
large uncertainty in RH (Swietlicki et al., 2008; Duplissy et al., 2009; Massling et al., 2011; Lopez-  
Yglesias et al., 2014). Controlling RH accurately inside the second DMA is also challenging. At RH  
= 95 % the most accurate chilled-mirror point hygrometer at typical accuracy of dew point  
60 temperature of  $\sim 0.1$  °C leads to an uncertainty in RH of  $\sim 0.6$  %. Uncertainties in HTDMA-derived  
growth factors can arise also from size bin width in the DMAs transfer function and from the offset  
in dry particle sizing between two DMAs (Swietlicki et al., 2008; Massling et al., 2011; Suda and  
Petters, 2013). Irregular structure of the initial dry particles leading to discrepancy between the  
65 mobility equivalent and mass equivalent particles diameters is an additional source of growth factor  
uncertainty (Mikhailov et al., 2004; Kreidenweis et al., 2005). The role of these sources of  
uncertainties increases significantly at RH > 90 %.

The desire to expand the upper RH bound in HTDMA experiments is mainly due bridge the  
gap between sub- and supersaturation conditions to provide data on aerosol-water interaction through  
65 the full range of relevant atmospheric saturation ratio (Kreidenweis et al., 2005). Of particular  
interest are non-ideal behavior of aerosol aqueous solutions at RH approaching to 100%, water  
activity-dependent hygroscopicity (Petters et al., 2009; Wex et al., 2009; Mikhailov et al., 2013, and  
size dependent partitioning effects between particle surface and volume (Ruehl et al., 2010).  
Understanding these phenomena and their quantification in the near-saturated air is relevant to

70 aerosol-radiation and aerosol-cloud interactions (Pöschl, 2005; Andreae and Rosenfeld, 2008; Pajunoja et al., 2015).

Two high humidity tandem differential mobility analyzers (HHTDMA) with an increased upper limit in RH are described in literature. The setup described by Hennig et al. (2005) allows growth factor measurement up to 98 % RH. In their setup, the second DMA was submerged in a temperature-controlled water bath. As a result, the temperature gradient inside the column was smaller than  $\pm 0.1$  °C. ~~However, due to RH was measured by dew point mirror ( $\pm 0.1$  °C) the resulting growth factor error at high humidity was significant. However, the resulting growth factor error at high humidity is significant since the RH was obtained using a dew point sensor.~~ Thus, at RH = 97.7 % the precision quoted by authors in absolute units is  $\pm 1.2$  % and particle growth factor relative uncertainty is 16.6 % ( $\pm 0.46$  at growth factor value of 2.79). For 100 nm dry ammonium sulfate aerosol, these uncertainties result in  $\pm 121$  % relative error in the retrieved hygroscopicity parameter (Suda and Petters, 2013).

The second HHTDMA setup was described by Suda and Petters (2013). This instrument allows for growth factor measurement up to 99% RH. In their setup, the first DMA was neither insulated nor temperature controlled. The second DMA was thermally insulated. The temperature gradient in DMA2 was estimated from column exterior temperatures and did not exceed  $\pm 0.02$  °C. At RH > 90 % they used calibration scans with ammonium sulfate to convert measured growth factors into RH using Extended Aerosol Inorganic model (E-AIM) (Clegg et al. 1998; Wexler and Clegg 2002). In this case, the precision in RH is  $\sim 1$  % at RH near 90 % and  $\sim 0.1$  % at RH of about 99 %.

~~The averaged in the 80–99 % RH range the relative growth factor uncertainty was 2.2 % (Suda and Petters, 2013, obtained from Fig. 2). The quoted uncertainty in measured hygroscopicity and activity coefficients is  $\pm 20$  %.~~ The resulting growth factor uncertainty associated with RH and instrumental errors is  $\sim 2\%$ , which is propagated in hygroscopicity and activity coefficients of  $\pm 20$  %.

~~Suda and Petters (2013) analyzed in detail the HHTDMA-based sources of uncertainty in the thermodynamic coefficients of organic aqueous solutions. They concluded that the size-dependent bin width of the DMA transfer function, the sizing offset between two DMAs, irregularities in the dry particles (shape factor) and controlled RH are the main factors responsible for the resulting uncertainty in the growth factor and thermodynamic coefficients, as a consequence. In addition to the HTDMA methods, other techniques have been used to determine the aerosol hygroscopicity at high RH (Tang et al., 2019). Two of these methods are the Leipzig Aerosol Cloud Interaction Simulator (LACIS; Stratmann et al., 2004) and the inverted streamwise-gradient cloud condensation nuclei counter (Ruehl et al. 2010), which could be operated at RH over the range of 85.8–99.1 % and 99.4–99.9 %, respectively. Both methods have accurate humidity control, but the optical detectors used to determine the wet particle size distribution are subjected to limitations~~

**Commented [E.M.1]:** Ref. #3 comment: Page 3, line 76: rephrase the sentence starting with "However, due to: : : . Text corrected (blue).

**Commented [E.M.2]:** Ref. #3 comment: Page 3, line 88: rephrase the sentence starting with "The averaged in the 80–99%... " Revised text in blue.

**Commented [E.M.3]:** Marked text has been deleted as it repeats the earlier text (Lines 50–62) and poorly synchronized with the suggestions of the Referee #2 (see next comment)

**Commented [E.M.4]:** Ref. #2 comment: The authors might consider adding a section comparing the versatility and accuracy of the system with other techniques. Specifically the Leipzig based LACIS instrument and the filter-based mass-based hygroscopicity method used by the same author previously would be interesting to compare in this context. New text is added (blue).

105 in accuracy resolution due to uncertainties in refractive index and the conversion from optical to physical diameter. This leads to uncertainty in the measured growth factors of  $\sim 4\%$  (Wex et al., 2005).

110 Mikhailov et al. (2011) developed a filter-based differential hygroscopicity analyzer (FDHA), which was employed as an offline method to investigate hygroscopic properties of ambient aerosol particles (Mikhailov et al., 2013, 2015). An updated version of the instrument allows measuring the hygroscopic growth up to 99.6 % with accuracy of  $\pm 0.1\%$  RH. The uncertainty in the determination of the mass growth factors was estimated to be  $\sim 1\%$  at 30 % RH and  $\sim 10\%$  at 99 % RH. FDHA measures water mass absorbed by aerosol particles deposited on the filters. Due to mass conservation, this method is not influenced by the effects of capillary condensation and restructuring of porous and 115 irregularly shaped particles that usually limit the applicability and precision of mobility diameter-based HTDMA and CCNC (Cloud Condensation Nuclei Counter) experiments. Since FDHA is katherometer-based technique, it takes on average of 2 days, to measure one aerosol sample, which is a drawback of this instrument.

120 Here we introduce a new HHTDMA instrument designed to overpass problems listed above such that the precision in growth factors in the 2–99.6 % RH range improved to  $\sim 0.6\%$  providing uncertainty in hygroscopicity and activity coefficients less than 4 %. We demonstrate these 125 uncertainties for glucose aerosol particles above and below water saturation.

## 2. Design of HHTDMA setup

125 Operating the HHTDMA at RHs above 99 % requires special operating procedures and temperature/humidity control systems. In this section, we describe the design of the various subsystems.

### 2.1 HHTDMA setup and operation modes

130 Figure 1 shows a sketch of the HHTDMA setup. Similar to conventional HTDMA system (Swietlicki et al., 2008; Duplissy et al., 2009) our setup consists of two DMAs (TSI 3081 type) connected in series with a humidity conditioning section between them. Both DMAs are housed in aluminum boxes and 135 thermally insulated with 20 mm polyethylene foam (Fig.S1.1). The temperature inside each aluminum box is actively controlled using a circulation thermostat (Lab. Companion, CW-05G) and two aluminum liquid heat exchangers (HRA120DR) with integrated fans. The DMA1 and DMA2 are operated at 26 °C and 25 °C, respectively. Two Pt100 needle sensors (uncertainty  $\pm 0.015\text{ }^{\circ}\text{C}$ .) placed in the sheath and excess airlines in DMA2 (T4, T5, Fig.1). The temperature difference between sheath and excess flow is small enough i.e. within Pt100 sensors uncertainty. The DM1 and DMA2 are operated with a closed loop sheath air setup. The sheath and aerosol flow rates in both DMAs were  $3.0$  and  $0.3\text{ l min}^{-1}$ , respectively.

140 The particle size distributions measured with the scanning mobility particle sizer (DMA 2, SMPS  
TSI 3080, CPC TSI 3772, TSI AIM version 9.0.0.0, Nov. 11, 2010) were fitted with a log-normal  
distribution function (Origin 9 software), and the modal diameter ( $D_b$ ) of the fit function were used for  
further data analysis.

145 In our setup, the RHs of the sheath and aerosol flow are separately adjusted. It is therefore possible  
to use three different modes of operation (Mikhailov et al., 2004; 2009):

1. “Hydration &dehydration” (*h&d*) mode (Mikhailov et al., 2004) or restructuring mode (Gysel  
et al., 2004) (Fig.1, red rectangle). This HHTDMA mode provides information about structural  
changes as a function of the relative humidity experienced during a cycle of humidification and  
drying (variable X = RH2; RH3, RH4 and RH5 <3 %). Here and below X represents the  
150 independent variable, i.e., the RH value taken for plotting and further analysis. The minimum  
mobility diameter observed in *h&d* mode ( $D_{h\&d,min}$ ) was used to approximate the actual mass  
equivalent diameter of dry particles ( $D_{m,s}$ ), which is a prerequisite for accurate Köhler model  
calculations.
2. “Hydration” HHTDMA mode provides information about deliquescence phase transitions of dry  
155 particles and the hygroscopic growth of deliquesced particles as a function of relative humidity  
(variable X= RH3 ≈ RH4 ≈ RH5; Fig.1).
3. “Dehydration” HTDMA mode provides information about the efflorescence transition of  
deliquesced particles and the hysteresis loop between deliquescence and efflorescence  
transitions as a function of relative humidity upon particle sizing after conditioning and  
160 deliquescence at high RH. The water filled pre-humidifier is set to a high RH (>96 %) (variable  
X = RH3 ≈ RH4 ≈ RH5; Fig.1).

165 The mobility equivalent particle growth factor,  $g_b$  was calculated as the ratio of the mobility  
equivalent diameter,  $D_b$  measured after conditioning (hydration, dehydration) to the minimum mobility  
diameter  $D_{b,h\&d,min}$  observed in *h&d* mode:  $g_b = D_b/D_{b,h\&d,min}$ .

## 2.2 Aerosol generation

170 Aerosols are generated by nebulizing ammonium sulfate (99.9 % pure, ChemCruz) or D-glucose  
(99.55% pure, Fisher) aqueous solution at ~0.01 % and ~0.1 % mass concentration, respectively.

Two separate atomizers operated with particle-free pressurized air (2.5 bar, 2 l min<sup>-1</sup>) are used. In the  
regular aerosol drying mode the generated solution droplets are first dried to a relative humidity of ~3  
% in the Nafion MD-700 (L = 60 cm), and then in the silica gel diffusion dryer (SDD, L = 100 cm ID  
= 2 cm, r.t. = 62.8 s). The MD-700 dryer operated at a purge air flow of 5 l min<sup>-1</sup> with input RH below  
0.3 %. The residual relative humidity at the exit of the SDD is <2% RH and close to that for sheath flow

175 in DMA1 (RH1, Fig. 1). The dry aerosol ( $0.3 \text{ l min}^{-1}$ ) is passed through a bipolar charger/radioactive  
neutralizer (Kr85) to establish charge equilibrium, and a differential mobility analyzer (DMA1) to select  
monodisperse particles. The used two-stage drying system (pre-dryer + SDD) provides the same  
humidity profile inside SDD throughout the HHTDMA experiment, which minimizes the effect of the  
drying conditions on the particle morphology and on the particle sizing as a consequence (Mikhailov  
180 et al., 2004; 2009; Wang et al., 2010).

### 2.3 Aerosol conditioning

185 The Nafion conditioning tube with inner diameter of 2.2 mm used for aerosol humidification in all  
HHTDMA operation modes. The length of H1, H2 and H3 Nafion conditioners is equal to 60, 120, and  
240 cm, respectively (Fig.1). In case of the H1 and the H3 exchangers, a  $1 \text{ l min}^{-1}$  humidified air flow  
passed through the outer tube to adjust the RH between 3% and 97 %. The humidity of the aerosol flow  
(RH3) and sheath air (RH4) in DMA2, is controlled by mixing water saturated and dry air flows in a  
ratio produced the desired RH. Saturated air is obtained by passing dry air through a Gore-Tex  
membrane tube submerged inside a temperature controlled water bath ( $27.0 \pm 0.1 \text{ }^{\circ}\text{C}$ ). Two separate 6  
190 mm (ID) Gore-Tex tubes, 0.5-m and 2-m long are used for aerosol and sheath flows conditioning,  
respectively (Humidifier, Fig. 1). For the H1 Nafion exchanger the humid air is prepared by bubbling  
air directly through water and then mixing with dry air to the required humidity (not shown in Fig.1). The  
outer shell of H2 Nafion tube is filled with pure water and thus set a RH greater than 96 %. For  
efflorescence HHTDMA mode the H1 and the H2 Nafion tubes are used in series (Fig.1). In the h&d  
195 HHTDMA mode aerosol in series flowed through a Nafion conditioner (H1, r.t. = 0.5 s), Nafion MD-  
700 dryer (L= 60 cm, r.t. = 27.2 s) and SDD (r.t. = 16 s) in which the RH of the aerosol is reduced to  
below 2 % (Fig.1, aerosol pre-conditioning section, red rectangle). The residence time between aerosol  
pre-conditioning system and DMA2 depends on the humidification mode; its minimum value is 6.5 s,  
which corresponds to r.t. in hydration operation mode (Fig.1). This is sufficient time to achieve an equal  
200 size at given RH, provided that there are no kinetic limitations to water uptake (Chuang, 2003;  
Mikhailov et al., 2004).

205 A 6mm (ID) Gore Tex membrane 2 m and 0.5 m long accordingly used for sheath air (RH4; DMA  
2) and aerosol flow (H3) humidification. The regulation of the humidity has been achieved by mixing  
saturated and dry air in variable proportions (Humidifier, Fig.1). The saturated air was obtained by  
bubbling air directly through water (not shown in Fig.1).

Commented [E.M.5]: Revised text

Commented [E.M.6]: Ref. #1 comment : *How did the GORE-TEX membrane work?*  
Ref. #3 comment: Page 5, line 172: rephrase the whole sentence, very unclear  
See revised text above (blue).

### 2.4 RH control

Relative humidity at several points throughout the apparatus is controlled by capacitive

210 sensors (RH1-RH5, Fig.1), supplemented with temperature ( $\pm 0.2$  °C) and atmospheric pressure sensors  
211 ( $\pm 2.5$  mbar). In addition, the RH inside of the DMA2 is determined by combining sheath air temperature  
212 and dew point temperature measured in the excess of airline (Fig.1). The accuracy of the dew point  
213 temperature is  $\pm 0.1$  °C, which in particular at 98 % RH leads an uncertainty of  $\pm 0.6$  % RH. All RH  
214 sensors and dew point mirror are periodically calibrated using the LI-610 dew point generator (LI-COR,  
215 USA). At RH  $> 90$  % due to instrumental limitations the RH measurement accuracy by capacitive RH  
216 probes and a dew point sensor drops noticeably. To circumvent this problem we used ammonium sulfate  
217 particles as a calibration standard. Based on the Extended Aerosol Inorganic Model (E-AIM, model II)  
218 (Clegg et al. 1998; Wexler and Clegg 2002), we converted the measured growth factors into RH  
219 ( $g_{b,E-AIM}$ ) (Rose et al., 2008; Suda and Petters, 2013; Rovelli et al., 2016). The uncertainty of water  
220 activity calculations with the E-AIM for aqueous solutions of ammonium sulfate above deliquescence  
221 relative humidity (DRH) (Clegg and Wexler, 2007) is better than  $10^{-4}$ , and is negligible relative to  
222 uncertainties of the growth factor measurement. Figure 2 shows the measurement uncertainty in RH by  
223 various methods. One can see that over a range of humidity levels the sensitivity of the methods is  
224 noticeably different. Therefore, to minimize uncertainty in the RH determination we used a dew point  
225 probe and capacitive sensors (RH4, RH5, Fig. 1) in the RH range of 5–80 %, and the HHTDMA-derived  
226 ammonium sulfate growth factors at RH above 80 %. Note that at RH below 80 % the E-AIM model  
227 parameters are based on the fit of electrodynamic balance (EDB) measurements, for which the accuracy  
228 in relative humidity is  $\sim 1$  % RH and in mass fraction of solute is about of  $\sim 1$  % (Chan et al., 1992;  
229 Clegg et al., 1995). For these uncertainties, the propagated growth factor error is  $\sim 1.0$  %, which exceeds  
230 instrumental growth factor error by a factor of  $\sim 5$  (see next section). Consequently, below deliquescence  
231 transition the RH accuracy was calculated accounting for EDB-based growth factor error (Fig.2, upper  
232 black curve), whereas above the deliquescence transition RH accuracy was obtained using instrumental  
233 growth factor uncertainty (Fig. 2, lower black curve).

## 2.5 Growth factor uncertainty

234 The instrumental growth factor error depends on uncertainty in particle sizing, which is result of  
235 variations in the flow rate, voltage, temperature, and atmospheric pressure. Uncontrolled change in these  
236 parameters causes a drift in dry mobility diameter and measured growth factor as a consequence.  
237 Regarding the precision of particle sizing by DMA1, the voltage variation from the specified value is  
238 less than  $\pm 1 \cdot 10^{-4}$  (HCE 7 -12 500, FuG Electronic), the relative standard deviation of the sheath flow is  
239 0.06 %. Unlike DMA1, where the critical orifice maintains a constant sheath flow, in the DMA2 the  
240 sheath flow is monitored by the microprocessor using temperature and pressure sensors built into mass  
241 flow meter. Our test measurements showed that within 10 hours, which is typical time scale of  
242 HHTDMA measurements, no trend in dry mobility diameter was observed (Fig.S.1.2). Over entire

period statistic error of the selected dry mobility diameter of 99.31 nm to be 0.16 nm ( $2\times\sigma_s$ ) which is  
 245 propagated in the instrumental relative growth factor error of  $\pm 0.002$  ( $\sigma_s$  is the standard deviation of selected dry mobility diameter). Nevertheless, to minimize systematic error caused by the casual drift of initial dry mobility diameter its size was measured at the beginning and at the end of every experiment.

We checked effect of width of the DMA2 transfer function on the uncertainty in particles sizing  
 250 by measuring the variability of the selected dry particles with diameters of 100, 200 and 300 nm. For these diameters based on six repeated measurements the relative uncertainty  $2\sigma_s/D$  was 0.0016; 0.0022 and 0.0015, respectively, indicating that the effect of transfer function broadening on the particle growth factor is negligibly small. However, variation in RH within DMA2 significantly affects the measurement precision of particle diameters, especially at high humidity. The RH-dependent measurement uncertainty in  $D_{b,RH}$  was fitted by the 3-parameter exponential function (Fig. S1.3):  
 255

$$\frac{2\sigma_{b,RH}}{D_{b,RH}} = \alpha + \beta \cdot \exp(\varepsilon \cdot RH) \quad (1)$$

Here  $\sigma_{b,RH}$  and  $D_{b,RH}$  are the standard deviation and particle mobility equivalent diameter at a given RH. The fit parameters ( $\alpha, \beta$  and  $\varepsilon$ ) obtained for ammonium sulfate and glucose aerosol particles are listed in supplement (S1). Finally, HHTDMA-derived growth factor uncertainty was calculated as follows:

$$\Delta g_b = \left( \left[ \left( \frac{2\sigma_s}{D_{b,s}} \right)^2 + \left( \frac{2\sigma_{RH}}{D_{b,RH}} \right)^2 \right] g_b^2 + \left( \Delta RH \frac{dg_b}{dRH} \right)^2 \right)^{1/2} \quad (2)$$

where the terms in square brackets describe the instrumental uncertainty of  $g_b$ , and the next term  
 260 accounts for the contribution of the RH sensor uncertainty to the particle growth factor. Note, when using Eq. (2) the  $dg_b/dRH$  was substituted by the measured  $\Delta g_b/\Delta RH$ .

We also checked the sensitivity of the SMPS inversion algorithm and log-normal fit to the ammonium sulfate particle size variations exiting DMA1. Figure 3a shows response of the SMPS classifier to a voltage (size) change in DMA1. It is seen that 1-volt step causes a proportional  
 265 displacement of the particle diameter by 0.12 nm (linear fit). Inset in Fig.3a indicates that this resolution significantly exceeds the size of individual bin (shown bin midpoints). As an example Fig.3b shows SMPS histogram of number particle distribution obtained for two DMA1 selected particles with  $\Delta = 3.9$  volt. It can be seen that voltage shift causes a change in particle concentration in each size bin, leading to a corresponding shift of the fitted size distribution and a change in modal particle diameter by 0.5 nm  
 270 as a result (insert in Fig.3b). Thus, the growth factor of near-monodisperse particles can be determined with higher precision than resolution of the size bins in the SMPS-derived histogram.

To eliminate the uncertainty in growth factors arising from the sizing offset between two DMAs (Massling et al., 2011) in our instrument the dry mobility diameter selected by DMA1 was measured by

275 the DMA2 on a par with the wet mobility diameter. However, additional uncertainty is introduced due to particle shape factor. As will be shown below, we managed to minimize this uncertainty using the restructuring mode.

### 3 Aerosol particles shape

280 Inorganic and organic aerosol particles as well as their mixtures restructure upon humidification below its deliquescence (Mikhailov et al., 2004, 2009; Biskos et al., 2006; Gysel et al. 2004). Irregular envelope shape and porous structure can cause a discrepancy between the mobility equivalent and mass equivalent particle diameters. To account for restructuring we use the minimum mobility particle diameter,  $D_{b,h\&d,min}$  obtained in *h&d* HHTDMA mode as an approximation of mass equivalent diameter of the dry solute particle,  $D_{m,s}$  i.e.  $D_{m,s} = D_{b,h\&d,min}$ . Based on *h&d* HHTDMA measurements 285 the dynamic shape factor,  $\chi$  of the dry initial particles can be estimated as following (DeCarlo et al., 2004):

$$\chi = \frac{D_{b,i} C(D_{b,h\&d,min})}{D_{b,h\&d,min} C(D_{b,i})} \quad (3)$$

290 where  $D_{b,i}$  is the initial mobility equivalent diameter selected by DMA1 and measured by DMA2,  $C(D_{b,h\&d,min})$  and  $C(D_{b,i})$  are the Cunningham slip correction factors for the respective diameters  $D_{b,h\&d,min}$  and  $D_{b,i}$  (Willeke and Baron, 1993).  $\chi$  can be split into a component  $\beta$  which describes the shape of the particle envelope and a component  $\delta$  which is related to the particle porosity and allows the calculation of the void fraction inside the particle envelope  $f$  (Brockmann and Rader, 1990):

$$\chi = \beta \delta \frac{C(D_{h\&d,min})}{C(D_{h\&d,min} \delta)} \quad (4)$$

$$f = (1 - \delta^{-3}) \quad (5)$$

## 4 Thermodynamic models

### 4.1 Full Köhler model

295 In this study, we used full Köhler model (Brechtel and Kreidenwies, 2000; Rose et al., 2008; Mikhailov et al., 2009) as a basis for HHTDMA calibration and for comparison to the measured growth factor-RH dependences:

$$\frac{RH}{100} = a_w \exp \left( \frac{4\sigma \bar{V}_w}{RTD_m} \right), \quad (6)$$

where  $a_w$  is the water activity,  $\sigma$  is the surface tension of the solution droplet,  $\bar{V}_w$  is the partial molar volume of water in solution,  $R$  is the ideal gas constant,  $T$  is the droplet temperature and  $D_m$  is the mass equivalent droplet diameter.

The partial molar volume of water in the droplet solution can be expressed by (Brechtel and Kreidenweis, 2000)

$$\bar{V}_w = \frac{M_w}{\rho} \left( 1 + \frac{X_s}{\rho} \frac{d\rho}{dX_s} \right), \quad (7)$$

where  $M_w$  is the molecular weight of water,  $\rho$  is the density of the solution, and  $X_s$  is the mass fraction of solute in the droplet.

The ratio of the aqueous droplet diameter,  $D_m$ , to the mass equivalent diameter of a particle consisting of the dry solute,  $D_{m,s}$ , is defined as the mass equivalent growth factor,  $g_m$ :

$$g_m = \frac{D_m}{D_{m,s}} = \left( \frac{\rho_s}{X_s \rho} \right)^{1/3}. \quad (8)$$

The concentration dependence of  $\rho$  for ammonium sulfate aqueous solution can be taken elsewhere (Tang and Munkelwitz, 1994). The density for glucose solution was obtained by the 2-nd order polynomial fit of the experimental data reported by Cerdeirina et al. (1997) ( $X_s < 0.5$ ) and Taylor and Rowlinson (1955) ( $X_s < 0.8$ ):

$$\rho(\text{g cm}^{-3}) = 1.0008 + 0.3477X_s + 0.1692X_s^2 \quad (9)$$

with standard deviation of the fit is 0.0021 g cm<sup>-3</sup>. The surface tension of the aqueous solution can be obtained using a simple linear approximation:

$$\sigma = \sigma_w + \sigma_{conc}[\text{Concentration}], \quad (10)$$

where  $\sigma_w = 72.0 \text{ mN m}^{-1}$  is the surface tension of pure water at 25°C and  $\sigma_{conc}$  account for the influence of the droplet composition and units of concentration. For ammonium sulfate  $\sigma_{conc} = 2.17 \text{ mN kg mol}^{-1}$  (molality-based) (Hänel, 1976) and for glucose solution  $\sigma_{conc} = 0.29 \text{ mN l mol}^{-1}$  (molarity-based) (Aumann et al., 2010). Solute molality,  $\mu_s$  (mol kg<sup>-1</sup>), solute molarity,  $C_s$  (mol l<sup>-1</sup>), molecular weight of solid,  $M_s$  (g mol<sup>-1</sup>), solution density,  $\rho$  (g cm<sup>-3</sup>), mole fraction of solute,  $x_s$ , mole fraction of water,  $x_w$  ( $x_w = 1 - x_s$ ), and mass fraction of solute,  $X_s$  are related by:

$$C_s = \frac{\mu_s \rho}{1 + \mu_s M_s / 1000}, \quad (11)$$

$$X_s = \left( 1 + \frac{1000}{\mu_s M_s} \right)^{-1}, \quad (12)$$

$$x_s = \frac{X_s / M_s}{X_s / M_s + (1 - X_s) / M_w}. \quad (13)$$

$$\mu_s = \frac{x_s \cdot 1000}{(1 - x_s) \cdot M_w} . \quad (14)$$

320 In the full Köhler model calculations  $a_w$  of the ammonium sulfate particles was taken from the Extended Aerosol Inorganics Model (E-AIM, model II) (Clegg et al. 1998; Wexler and Clegg, 2002) and the corresponding molality  $\mu_s$  was obtained. Alternatively, water activity of the glucose solution droplets was obtained from relation:

$$a_w = \gamma_w x_w , \quad (15)$$

325 where water activity coefficient,  $\gamma_w$  calculated from two-suffix Margules equation (Taylor and Rowlinson, 1955):

$$\ln \gamma_w = -Ax_s^2, \quad (16)$$

330 with  $A = -1.957 (\pm 0.062)$ . Note, there are also other theoretical equations such as three-suffix Margules equation (Cindio and Correra, 1995; Miyawaki et al., 1997), but the difference in the  $\gamma_w$  calculated values between Eq. (16) and more complicate expressions is negligibly small within  $\sim 0.01\%$ . Equations (6–16) can be used to model the hygroscopic growth of aerosol particles, i.e., to calculate  $g_m$  and  $D_m$ , respectively, as a function of  $D_{m,s}$  and  $RH$ .

#### 4.2 Growth factor and hygroscopicity parameterization

As proposed by Kreidenweis et al. (2005), hygroscopic growth data points can be approximated with a polynomial 3-paramter fit function of the following form:

$$g_b = \left( 1 + [k_1 + k_2 a_w + k_3 a_w^2] \frac{(1 - a_w)}{a_w} \right)^{1/3}. \quad (17)$$

335 Using Eq.(6) we convert the measured RH-based growth curves ( $g_b$  vs. RH) into water activity growth curves ( $g_b$  vs.  $a_w$ ) assumed that  $D_{b,h\&d,min} = D_{m,s}$ ,  $\bar{V}_w$  and  $\sigma$  equal to the partial molar volume and surface tension of pure water, respectively. For pure glucose aerosol particles, the relative errors introduced by this simplifying assumption in the calculation of  $a_w$  from Eq. (6) were less than 0.1%.

340 According to Petters and Kreidenweis (2007), the hygroscopic properties of aerosol particles can be approximately described by a single hygroscopicity parameter,  $\kappa$  :

$$a_w = \frac{D_m^3 - D_{m,s}^3}{D_m^3 - D_{m,s}^3(1 - \kappa)}, \quad (18)$$

Under the assumption of volume additivity, Eq. (18) can be rewritten as:

$$\kappa = \frac{(g_m^3 - 1)(1 - a_w)}{a_w} . \quad (19)$$

As a result, the hygroscopicity  $\kappa$  can be determined from each HHTDMA-measured data pairs of  $g_m$  vs.  $a_w$  under the assumption  $g_b = g_m$ . For ideal solution, Raoult  $\kappa$ ,  $\kappa_R$  can be calculated using known constants (Rose et al., 2008; Mikhailov et al. 2009);

$$\kappa_R = v_s \frac{M_w \rho_s}{M_s \rho_w} , \quad (20)$$

345 where  $v_s$  is the stoichiometric dissociation number of solute.

#### 4.3 Molal osmotic coefficient

According to Robinson and Stokes (1970) the molal osmotic coefficient of solute in aqueous solution,  $\Phi_s$  can be obtained from relation:

$$\Phi_s = - \frac{1000 \ln a_w}{v_s \mu_s M_w} . \quad (21)$$

350 For hydrophilic nonelectrolytes ( $v_s = 1$ ) nonideality is caused by hydration of solutes. As proposed by Rudakov and Sergievski (2009) for such aqueous solutions the activity coefficient of water can be estimated according to the equation:

$$\ln \gamma_w = 2h^0(\ln x_w + x_s) , \quad (22)$$

where  $h^0$  is the hydration number of the solute at  $x_w = 1$ . From Eq.(15) and Eq.(22) it follows:

$$\Phi_s = - \frac{x_w}{1 - x_w} (\ln x_w + 2h^0[\ln x_w + (1 - x_w)]) . \quad (23)$$

355 **4.4 HHTDMA-derived activity coefficients**

In a binary system at constant temperature and pressure, the activity coefficient of water,  $\gamma_w$  and activity coefficient of solute,  $\gamma_s$  are related by the Gibbs–Duhem equation:

$$x_w d \ln \gamma_w + x_s d \ln \gamma_s = 0 . \quad (24)$$

360  $x_w$  can be obtained based on HHTDMA-derived aerosol particle growth factors. First simple method is based on volume additivity assumption when the volume of the solution droplet is given by the sum of the volumes of the dry solute and of the pure water contained in the droplet (Mikhailov et al., 2009; Petters et al., 2009):

$$\frac{1}{x_w} = 1 + \frac{\rho_s M_w}{\rho_w M_s} (g^3 - 1)^{-1} . \quad (25)$$

365 ~~If the concentration dependence of the solution density is known, then  $x_w$  can be obtained without assumption of volume additivity by iteratively solving Eq. (8) with other equation where  $\rho$  and concentration is given explicitly.~~ For many atmospheric aerosols, the concentration dependence of the aqueous solution density is not well defined. At the same time, for a number of model systems of interest, the aerosol solution density was measured in both unsaturated and supersaturated solutions. In  
 370 this case  $x_w$  can be obtained without assumption of volume additivity by iteratively solving Eq. (8) with other equation where  $\rho$  and concentration is given explicitly. For example, Eq. (9) was used for glucose solution droplets. The mass fraction,  $X_s$  calculated in this way for a given  $g_m$  was then converted into  $x_w$ , using Eq.(13).

375 The activity coefficient,  $\gamma_s$  of glucose in water solution was obtained by numerical integration of Eq.(24) using EXPGro3 function (Origin 9 software) to fit and then integrate experimental dependence of  $x_w/x_s$  vs.  $\ln\gamma_w$ . The boundary conditions are based on asymmetric reference system: at  $x_s \rightarrow 0$ ;  $\gamma_w \rightarrow 1$ ,  $\gamma_s \rightarrow 1$ , i.e., at  $x_s = 0$ ;  $\ln\gamma_w = 0$  and  $\ln\gamma_s = 0$ . Integration yields:

$$\ln\gamma_s(\text{at } x_s) = -[F(\ln\gamma_w \text{ at } x_s = x_s) - F(\ln\gamma_w = 0 \text{ at } x_s = 0)] \quad (26)$$

380 Using Eq. (15) the received  $\gamma_s$  can be easily converted into the solid activity,  $a_s$ . Thus, relying only on known solution density, the thermodynamic parameters  $x_w$ ,  $\gamma_w$ , and  $a_w$  as well as  $x_s$ ,  $\gamma_s$ ,  $a_s$  and  $\phi_s$  can be obtained from the HHTDMA-measured  $g_b(RH)$  dependence without assumption of volume additivity. This is important for concentrated droplet solution where volume additivity is not always hold.

#### 385 4.5 Surface adsorption

The amount of water adsorbed on the surface of crystalline aerosol particles prior to deliquescence can be described with surface coverage ( $\Theta$ ) (or number monolayers on dry particles surface). Assuming that initial particles are compacted and spherical, the number monolayers can be calculated from the ratio:

$$\Theta = \frac{D_{RH} - D_{m,s}}{2D_w}, \quad (27)$$

390 where  $D_w$  is the diameter of adsorbed water molecule (0.277 nm) (Yeşilbaş et al., 2016). The FHH (Frenkel, Halsey and Hiil) model is the frequently used to relate surface coverage to a water activity:

$$a_w = \exp(-A_{FHH}/\Theta^{B_{FHH}}), \quad (28)$$

**Commented [E.M.7]:** Ref.#2 comment: *The authors state that activity coefficients can be determined from the data without the need to assume volume additivity by relying only on known (bulk) solution density. The authors should add that solution density is rarely known for metastable solutions and systems of interest to be studied with the HHTDMA.*

Added (blue)

where parameter  $A_{FHH}$  characterizes interactions between adsorbed molecules in the first monolayer and between the surface, and  $B_{FHH}$  characterizes the attraction between the solid surface and the adsorbate in subsequent layers. ...where AFHH and BFHH are empirical fit parameters that describe the intermolecular interactions governing the adsorption potential.  $A_{FHH}$  characterizes interactions between the surface and first adsorbed water layer as well as interactions between adjacent molecules.  $B_{FHH}$  describes the interactions between the surface and subsequent adsorbate layers. Inserting Eq.

**Commented [E.M.8]:** Ref. #1 comment: Page 13, Line 358-360: This sentence is obscure and should be rewritten.  
Updated sentence in blue.

395 (28) into Köhler model (Eq. 6) the parameters  $A_{FHH}$  and  $B_{FHH}$  can be estimated (Romakkaniemi et al.,  
400 2001; Sorjamaa and Laaksonen, 2007; Hatch, et al., 2019).

## 5 Experimental results and discussion

### 5.1. Aerosol particle restructuring

The hydration&dehydration (h&d) HHTDMA operation mode was first used to study effect of the drying condition on the aerosol particle restructuring. Specifically, in the aerosol generation section (Fig.1) we alternatively used the Nafion MD -700 dryers of various lengths providing residence time of the aerosol flow in the range of 27–62 s, solely the silica gel diffusion dryer (SDD) with r. t. = 62 s, and a coupled drying system, comprising the Nafion MD -700 and the SDD dryers. The dried aerosol particles selected by DMA1 entered to the pre-conditioning section (Fig.1, red rectangle), where during a cycle of humidification (H1, r.t. = 0.5 s) and drying (Nafion MD 700, r.t. = 27 s; SDD, r.t. = 16 s) they underwent microstructural transformation, as previously described in Mikhailov et al. (2004; 2009).

#### 5.1.1 Ammonium sulfate particle

Figure 4a shows the change in the initial dry mobility diameter of 100.3 nm ammonium sulfate aerosol particles obtained at different drying conditions. In the range of 2–60 % RH the mobility diameter gradually decreases, and when RH is more than 70 % RH it becomes almost constant with  $D_{b,h\&d,min}$  observed at 80–90% RH. The  $D_{b,h\&d,min}$  values obtained for all drying modes are shown in Table 1.

Interestingly, when using only MD-700 dryer the variation in the r.t. from 27 to 67 seconds leads to a decrease in the  $D_{b,h\&d,min}$  by only 0.4 nm (i.e. at r.t. = 27 s,  $D_{b,h\&d,min} = 98.4$  nm; at r.t. = 67 s,  $D_{b,h\&d,min} = 98.0$  nm). A sharp decrease in minimum mobility diameter by ~ 3 nm ( $D_{b,h\&d,min} = 95.3$  nm) occurs when SDD (r.t. = 62 s) is added to the MD-700 membrane dryer (r.t. = 27 s), that is already effloresced aerosol particles (RH ~ 3% at the outlet of the MD-700 dryer) ~~undergo~~ underwent further microstructural changes inside SDD. The maximum reduction (by ~7 nm) of the initial DMA1 selected particles is observed when only SDD is used as a desiccant, at which  $D_{b,h\&d,min} = 93.2$  nm and 93.5 nm (first and second run with the same SDD, Fig.4a).

Multiple Köhler model calculations based on  $D_{b,h\&d,min}$  obtained in all used drying modes are in excellent agreement with the observed hygroscopic growth curves. These findings confirm the compactness and spherical shape of dry particles, despite the fact that the absolute values of  $D_{b,h\&d,min}$  are different and strongly depend on the drying conditions (Fig.4a).

430 The different values of  $D_{b,h\&d,min}$  observed upon *h&d* mode is a result of different microstructure of the initial dry particles having the same  $D_{b,i}$  (Table 1). As previously noted the dry particle morphology depends on drying rate (Zelenyuk et al. 2006, Zhao et al., 2008; Mikhailov et al., 2009; Wang et al, 2010), since the solidification of aerosol droplets is mainly governed by kinetic rather than thermodynamic factors. Experiments with MD - 700 membrane dryer show that at the same drying rate,

435 the residence time has a little effect on ammonium sulfate particle morphology, i.e. an increase in the r.t. from 27 to 67 s., the dynamic shape factor slightly grows from 1.033 to 1.040 (Table 1). The obtained in this experiment values are close to those reported by Kuwata and Kondo (2009), who used the combination of a DMA and an APM (aerosol particle mass analyzer) system. They estimated that  $\chi$  of  $(\text{NH}_4)_2\text{SO}_4$  for 50-150 nm is 1.01 ~ 1.04. Zelenyuk et al. (2006) using DMA and single-particle laser 440 ablation time-of-flight mass spectrometer (SPLAT) measurements showed that  $\chi$  is  $1.03 \pm 0.01$  at 160 nm. Biskos et al. (2006) estimated a  $\chi$  for 6 – 60 nm  $(\text{NH}_4)_2\text{SO}_4$  particles of 1.02, based on the observed particles restructuring in the hydration HTDMA mode. Our  $\chi$  values obtained with MD - 700 membrane dryers and those that preliminary reported most likely reflects surface irregularities as observed by **SEM** (Scanning Electronic Microscope) (Fig.5A) and **TEM** (Transmission Elcronic microscope) **electron**

445 **microscope** (Dick et al, 1998; Zelenyuk et al., 2006). At the same time, an experiment with serially connected dryers (MD -700 + SDD) indicates that after first dryer effloresced particles still contain liquid. The liquid could be located in cavities with various degrees of shielding (Cohen et al., 1987; Weis and Ewing, 1999; Colberg et al., 2004). Figure 6 outlines possible structures of aerosol particles and their microstructural rearrangements during *h&d* experiment. Based on the experimental results 450 considered above, we can assume that in membrane dryers (MD-700) the effloresced particles release surface water and water that is stored in relatively open cavities, providing an irregular aerosol particles envelope (Fig.5A) (also Dick et al., 1998, see Fig. 7). However, part of liquid remains in either completely closed or partially shielded cavities. The latter can be pores, veins, and grain boundaries, that retain water due to inverse Kelvin effect on concave surfaces (Fig. 6, pattern I) thereby impeding 455 exchange between gas phase and the cavities. The fresh SDD added to membrane dryer overcome diffusion barrier created by capillary forces most likely due to drying rate in SDD is much faster than that in membrane dryer. As a result, some of partially shielded cavities release excess water. Note this process is accompanied by further microstructural rearrangement, leading to formation porous aerosol particles (Fig.6, pattern II) with  $D_{b,h\&d,min}$  is smaller than that observed after membrane dryer ( $\sim 95.3$  460 nm vs.  $\sim 98.4$  nm, Table 1). Accordingly, the aerosol particle shape factor,  $\chi$  increases from  $\sim 1.03$  to  $\sim$

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AC

We have added the SEM images of initial ammonium sulfate and glucose aerosol particles (Fig. 5) in order to strengthen the argument in favor of the discussed aerosol particles morphology and the calculated values of particle shape ( $\chi, \beta$ ) and porosity ( $\delta, f$ ) presented in Table 1.

**Commented [E.M.10]:** New Fig. 5A is added.

1.09 (Table 1). Finally, more porous particles are formed when solely fresh SDD is used as a desiccant ( $D_{b,h\&d,min} = 93.3$  nm,  $\chi = 1.13$ ; Table 1). As pointed out before (Mikhailov et al., 2009; Wang et al., 2010) excess charge and rate of drying are important for microstructure of aerosol particles generated by nebulization of aqueous solution. Most likely in case of fresh SDD the most porous/irregular

465 particles (Fig.6, pattern III) forms due to strong kinetic limitations arising at a sufficiently rapid drying inside SDD. More pronounced multiple nucleation events could occur by increasing the number of polycrystals and accordingly the number and scale of cavities. As a result, at the same  $D_{b,i}$  the observed  $D_{b,h\&d,min}$  of re-dried particles (*h&d* mode) is strongly dependent on the drying conditions (Fig.6; Table 1, the last column).

470 Assuming that the  $\chi$  value obtained in the experiment with the membrane dryer accounts for the aerosol particles envelope, i.e.  $\chi = \beta = 1.033$  (Fig. 5A) and using Eq.(4) and Eq.(5) we estimated the

Commented [E.M.11]: Dew to Fig. 5 is added

475 particle porosity,  $\delta$  and void fraction,  $f$ , respectively. The calculated values of the particle void fraction for the coupled (MD 700 + SDD) drying system and for the single SDD are  $\sim 9\%$  and  $\sim 14\%$ , respectively (Table 1). Obviously, this difference reflects the effect of drying conditions on particle morphology as discussed above. Since in the two-stage drying system, the microstructural rearrangement of particles inside SDD occurs due to the remaining water the obtained  $f \approx 9\%$  can be attributed to the volume fraction of water stored in pores and veins after first drying stage (Fig.6 pattern I). In the mole fraction basis the water content in the dry solid aerosols can be obtained from:

$$\frac{n_w}{n_s} = (\delta^3 - 1) \frac{\rho_w M_s}{\rho_s M_w}. \quad (29)$$

480 According to Eq. (29) the  $\text{H}_2\text{O}:(\text{NH}_4)_2\text{SO}_4$  molar ratio,  $(n_w/n_s)$  in the dry particles after membrane dryer is  $\sim 0.4$  (0.41 and 0.39 for the first and second run). In case of the one-stage of aerosol drying when only SDD is used the volume fraction of  $\sim 14\%$  corresponds to  $\text{H}_2\text{O}:(\text{NH}_4)_2\text{SO}_4$  molar ratio of  $\sim 0.7$  (0.69 and 0.73 for the first and second run). This value can be considered as an upper limit of the water content, since it is assumed that all cavities are filled with water. The  $\text{H}_2\text{O}:(\text{NH}_4)_2\text{SO}_4$  molar ratio range of 0.4–0.7 obtained in this study at  $\text{RH} < 3\%$  is close to that reported by Weis and Ewing

485 (1999) for submicron NaCl aerosol particles with median diameter of 350 nm. In their FTIR spectroscopic flow tube experiment for  $\text{RH}$  of 15–5 % the obtained  $\text{H}_2\text{O:NaCl}$  molar ratio in the silica gel dried particles varies between 0.5 and 0.7. They suggest that during the crystallization process water is present in open and shielded pockets.

#### 490 5.1.2 Glucose particles

Figure 4b shows mobility equivalent diameter observed upon *h&d* mode of glucose aerosol particles. Unlike ammonium sulfate (Fig.4a), the minimum mobility diameter of the glucose aerosol particles is

already observed at  $\sim 20\%$  RH. Moreover,  $D_{b,h\&d,min}$  was practically independent of drying conditions. Accordingly, the shape factor calculated from Eq. (3) is also constant ( $\chi=1.06$ ; Table 1). **Atomic force microscopy analysis performed by Estilliry et al. (2017)** SEM images (Fig.5B) indicate that  $\sim 100$  nm glucose particles as well as other sugars are perfect spheres therefore, one can assume that  $\beta=1$ . From Eq. (4) and Eq.(5) it follows that  $\delta \sim 1.03$  and  $f \sim 10\%$  (Table 1). The fact that particle restructuring does not depend on the residence time and type of dryer indicates a lower energy barrier to the water transport from the cavities to ambient air as compared to the ammonium sulfate particles. As will be shown below glucose aerosol particles like other monosaccharides tend to reversible water uptake starting at very low RH, which is typical for particles with an amorphous structure (Fig.6, pattern IV) (Mikhailov et al., 2009; Koop et al., 2011). The absorbed water acts as a plasticizer, which soften the microstructural rearrangements inside swelling particles (Fig. 6). Moreover, at low RH the water uptake is facilitated by presence of alcohol functional groups within sugars that form hydrogen bonds with water. These effects can explain why in contrast to ammonium sulfate, restructuring of the glucose aerosol particles starts at low humidity and practically completed at  $\sim 20\%$  RH. A slight increase in  $D_{b,h\&d}$  observed at RH above  $20\%$  RH (Fig. 4b) is probably due to high hygroscopicity of glucose and low diffusivity of water molecules through a (semi)-solid matrix of the compacted particles (Fig. 6) (Shiraiwa et al., 2013). However, the fact that in case with glucose aerosol particles the drying conditions do not have a significant effect on  $D_{b,h\&d,min}$  is not entirely clear. Further work is needed to clarify this effect.

One of the most important structural metrics of a porous material is the connectivity of the pore space, or the so-called pore network. This has bearing on the diffusive tortuosity and permeability of water. Most of the pores are connected to each other as well as to the surface via small throats (open pores), whereas some pores are shielded from the connected structure. According to estimates, the fraction of voids in the aerosol particles of ammonium sulfate and glucose obtained under the same drying conditions are comparable (Table 1). However, pore network can be different. It is possible therefore, that in amorphous glucose the pore network has more open pores than in case of polycrystalline ammonium sulfate particles, leading to a more efficient exchange of water between filled cavities and gas phase at the same drying conditions.

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The conclusion about the difference in the porous structure of ammonium sulfate and glucose particles is based on the results of HHTDMA measurements in the h&d mode. To our knowledge, there are no direct methods for measuring the pore network of 100 nm particles. SEM is a useful technique for extracting two-dimensional (2D) images of the microstructures but does not provide the third spatial component of the sample, which is important to find interconnected regions and pore volumes, shapes and sizes. We have added the SEM images of initial ammonium sulfate and glucose aerosol particles (Fig. 5) in order to strengthen the argument in favor of the discussed aerosol particles morphology and the calculated values of particle shape ( $\chi, \beta$ ) and porosity ( $\delta, f$ ) presented in Table 1.

## 5.2 Hygroscopic growth

To avoid the uncertainties associated with the aerosol particles morphology, we combined h&d mode with one of the hygroscopic growth mode. That is before aerosol particle humidification (hydration, dehydration) the dry aerosol particles selected by DMA1 first entered to the pre-conditioning (PC) section (Fig.1, red rectangle) where they underwent microstructural rearrangements forming more

compact and near-spherical particles. In the PC section, relative humidity (RH2, Fig.1) was maintained in the range of 80–90 % and ~ 20 % for ammonium sulfate and glucose aerosol particles, respectively. These RH values correspond to  $D_{b,h\&d,min}$  obtained in h&d mode (Fig.4) which is a good approximation 530 of mass equivalent diameter of dry particles.

### 5.2.1 Ammonium sulfate water uptake prior to deliquescence.

Figure 7 shows the change in the initial mobility diameter of ammonium sulfate particles observed in hydration mode before deliquescence transition. It is seen that particles with and without pre- 535 conditioning demonstrate different response to changes in RH. The particles that bypass pre-conditioning step due to irregular/porosity microstructure undergo a strong restructuring ( $D_{b,i}$  decreased by 4.3 nm), while pre-conditioned particles (h&d mode) exhibit a small but continuous hygroscopic growth. Assuming that initial pre-conditioning particles are compact and spherical (i.e  $D_{b,i} = D_{b,h\&d,min} = D_{m,s}$  and using Eq. (27) we have converted the difference between the mobility diameters observed 540 in hydration mode into an equivalent number of monolayers. As illustrated in Fig. 7 we obtained near liner growth of  $\Theta$  from ~ 0 to 3.5 for the range of 5–75 % RH and sharp increase up to  $\Theta \sim 6$  over the range of 75–79 % RH. The findings are consistent with our earlier HTDMA studies of water adsorption on ammonium sulfate particles (Mikhailov et al.2009) and with the literature data considered therein. The obtained  $\Theta(RH)$  dependence was fitted using Eq. (6) with water activity taken from FHH isotherm 545 Eq. (28). Calculations were performed assuming that  $\sigma$  and  $\bar{V}_w$  parameters equal to those for pure water. The fit result is shown in Fig. 7 (solid line). The best fit parameters are  $A_{FHH} = 1.07 \pm 0.08$  and  $B_{FHH} = 0.94 \pm 0.07$ . Romakkaniemi et al. (2001) also used HTDMA measurements with NaCl and  $(\text{NH}_4)_2\text{SO}_4$  particle between 8 and 15 nm to estimate  $\Theta$  before deliquescence transition. For ammonium sulfate 550 particle calculated parameters for FHH isotherm are  $A_{FHH} = 0.68$  and  $B_{FHH} = 0.93$ . The  $A_{FHH}$  value obtained in our work is ~40 % higher than that reported by Romakkaniemi et al. (2001). One possible explanation is that the surface coverage is lower on surfaces of nano-sized particles compared to flat surfaces (Müller et al., 1987). Another and perhaps more important reason is that Romakkaniemi et al. (2001) used initial mobility diameter,  $D_{b,i}$  for  $\Theta$  calculation without particles shape correction. Biskos 555 et al. (2006) have shown that nano-sized ammonium sulfate particles in range of 6 - 60 nm undergo a restructuring upon RH increasing. Thus for 6 – 8 nm particles the minimum mobility diameter observed in the 30 – 60 % RH range is by ~2 % lower than initial mobility diameter, that corresponds to the uncertainty in  $\Theta$  about ~1 monolayer of adsorbed water (see Eq.27). This explains why the Romakkaniemi et al. (2001) data of  $\Theta$  are lower than that obtained in this study.

The water uptake before particles deliquescence was detected in earlier studies (Weingartner et

560 al., 2002; Gysel et al., 2002; Biskos et al., 2006), but it was observed mainly at RH >70 %. Most likely

restructuring, which occurs upon particles hydration has masked water uptake at low RH. Experimental  $D_b$  (RH) dependence obtained for non-pre-conditioning particles (Fig.6, open circles) clearly demonstrate this effect. Alternatively, the hygroscopic growth data obtained for pre-conditioning particles with compact structure (Fig.7, closed circles) shows that the water adsorption on the surface 565 of the solid particle occurs already at lower humilities, ranging from ~15 % RH.

### 5.2.2 Ammonium sulfate hydration and dehydration.

Figure 8 shows growth factors of the pre-conditioned ammonium sulfate particles with  $D_{b,h\&d,min} = 79.6$  570 nm obtained upon hydration and dehydration HHTDMA modes at 298 K. The observed efflorescence RH (ERH =  $34.8 \pm 0.2$  %) and deliquescence RH (DRH =  $79.9 \pm 0.2$  %) are within literature data obtained for submicron ammonium sulfate particles (Mikhailov et al., 2009; Gao et al., 2006; Ciobanu et al., 2010; and references therein).

The experimental growth factors are compared to a full Köhler model with water activity parameterization derived from the E-AIM II (Clegg et al. 1998; Wexler and Clegg 2002). As illustrated in Fig.8a up to 97% RH the HHTDMA experimental data are in very good 575 agreement with model growth factors. Insets in Fig.8a shows the experimental growth factor uncertainties which gradually go up due to increase of the RH uncertainty (Eq. 2, terms  $2\sigma_{RH}/D_{b,RH}$  and  $\Delta RH(dg_b/dRH)$ ). Averaged over the range of 38–96 % RH, the mean ~~relative~~ deviation between measurement and model results ~~were is~~ < 0.5 %. The good agreement between model and measurement results confirms that the ammonium sulfate particles with  $D_{b,h,min}$  are compact and spherical (i.e.  $D_{b,h,min} = D_{m.s.}$ ). However above ~97 % RH due to sharp growth of the  $\Delta RH(dg_b/dRH)$  term in Eq. (2) the 580 observed growth factors are systematically deviate from Köhler model. Thus at ~98 % RH this deviation is ~ 7 %, and at 99.5 % RH it is already ~15 % (insert in Fig.8a).

Figure 8b shows the measured growth factors, which were converted into RH using E-AIM at 585 RH above deliquescence transition. In this case, the RH accuracy is determined by the instrumental growth factor error (Eq. 2, terms in square brackets). Insets in Fig.8b indicate that RH accuracy progressively improves with RH increasing. Thus at 85% RH absolute accuracy is  $\pm 0.3\%$ , while at 99.5% RH it is only  $\pm 0.03\%$  (Fig. 2). Thus, using experimental ammonium sulfate growth factors, it is possible to eliminate RH uncertainty generated by capacitive and dew point sensors at RH above 80%.

Overall, the combination of two HHTDMA operation modes (h&d and hydration/dehydration) 590 that eliminate the effect of particle shape factor, and precise determination of RH using ammonium sulfate, is a prerequisite for accurate determination of the thermodynamic parameters of aerosol particles in the wide range of RH. In the next section, we will show the effectiveness of this approach by the example of glucose aerosol particles.

595 **5.2.3 Glucose hydration and dehydration**

Figure 9a shows mobility equivalent growth factor observed upon hydration and dehydration of pre-conditioned glucose aerosol particles with  $D_{b,h\&d,min} = 99.6$  nm observed upon hydration and dehydration HHTDMA operation modes. In both modes, over the 2 - 99.6 % RH range the change in the growth factor occurred gradually. In contrast to (poly-) crystalline ammonium sulfate (Fig.8a), no stepwise changes in  $g_b$  associated with DRH and ERH phase transitions is observed. Such behavior is typical for particles with amorphous structure as earlier discussed in Mikhailov et al. (2009). In general, growth factors obtained in hydration and dehydration experiments are in a good agreement with those previously reported by Mochida and Kawamura (2004) and Suda and Petters (2013). Nevertheless, a slight positive deviation of ~ 1% can be traced throughout the all RH range. Growth factors presented by Mochida and Kawamura (2004) and Suda and Petters (2013) were calculated without particle shape correction. As noted in Sect.5.1.2 due to porosity the glucose aerosol particles undergo a wet restructuring decreasing their initial mobility diameter (Fig.4b; Table 1)). Therefore, using  $D_{b,i}$  instead of  $D_{b,h\&d,min}$  as an approximation of mass equivalent diameter of the dry solute particle  $D_{m,s}$  may lead to underestimated values of the growth factor (Eq.8).

610 Figure 9b shows the change in the total relative uncertainty of the growth factor caused by RH and instrumental uncertainties. A small drop in growth factor uncertainty observed at ~80% RH (blue curve) is caused by replacing of the RH control method (Sect.2.4) and its decrease above ~97% RH is due to a sharp drop in  $\Delta RH$  ( $g_{b,E-AIM}$ ) near water saturation (Eq. (2); Fig.2). On the contrary, the instrumental  $g_b$  uncertainty increases monotonously (Fig.9b, red curve) due to the smooth growth of the RH dependent the  $\sigma_{b,RH/D_{b,RH}}$  ratio in Eq. (1) (Fig. S1.3).

615 Figure 10 shows the HHTDMA growth factors as compared to full Köhler model (Eq.6) with  $a_w$  calculated from Eq.(15) using bulk water activity coefficient,  $\gamma_w$  from Taylor and Rowlinson (1955) (Sect.4.1), and  $\bar{V}_w$  and  $\sigma$  calculated from Eq.(7) and Eq.(10), respectively. Excellent agreement between HHTDMA-based and full Köhler model data is observed: throughout the 91.0 - 99.6% RH range average deviation of the experimental data points from the model is 0.7%. The observed coincidence indicates that  $D_{b,h\&d,min}$  value obtained upon restructuring is a good approximation of mass equivalent diameter of the dry glucose aerosol particle, i.e.  $D_{b,h\&d,min} \approx D_{m,s} = 99.6$  nm. It also confirms the small growth factor uncertainty associated with RH and instrumental  $g_b$  errors, which is in the range of 0.3-0.9% throughout the all 2 - 99.6% RH interval (Fig.9b, black curve).

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### 5.3 Glucose thermodynamic variables

#### 5.3.1 Water activity and hygroscopicity parameter

Using Eq. (6) the experimental  $g_b$  vs. RH data points were converted into data pairs  $g_b$  vs.  $a_w$  (Sect. 4.2). Figure 11a shows the obtained activity-based growth factors, which were fitted with Eq.(17) to 630 determine best-fit values of the parameters  $k_1$ ,  $k_2$  and  $k_3$  (Table 2). Figure 11a also illustrates the difference between experimental data points and ideal solution model, which traced throughout the all water activity range (inserts in Fig.11a) with maximal deviation of 3.6% at  $a_w \approx 0.8$ . Only at  $a_w > 0.98$  the experimental growth factors coincide with the ideal model within uncertainty of  $g_b \sim 0.6\%$ . For ideal 635 solution model the  $g_b(a_w)$  dependence was calculated from Eq.(25) with  $a_w = x_w$ . Note, given Eq.(20) for  $\kappa_R$  the Eq.(25) can be reduced to:

$$g_{b,ideal} = \left(1 + \kappa_R \frac{a_w}{1 - a_w}\right)^{1/3}, \quad (30)$$

which is an analog of Eq.(19) where  $\kappa = \kappa_R$ .

For each experimental  $g_b$  vs.  $a_w$  data pairs we have calculated  $\kappa$  values using Eq.(19). Inserting fitted values of  $g_b(a_w)$  into Eq.(19) we have obtained the corresponding fit curve for activity-based 640 hygroscopicity,  $\kappa$ . The obtained results are shown in Fig. 11b. Due to concentration effects (Mikhailov et al., 2013 and references therein) hygroscopicity parameter decreases with  $g_b$  increasing. At  $a_w > 0.98$  the  $\kappa$  becomes almost constant. In this area the estimated value of  $\kappa$  is  $0.160 \pm 0.006$  (average of the 10 data points  $\pm$  propagated uncertainty; see insert in Fig.11b), which is close to the ideal solution value of  $\kappa_R = 0.154$  (Eq.20). The hygroscopicity  $\kappa$  obtained in this study for dilute glucose solution is in 645 agreement with that derived by Ruehl et al. (2010) ( $\kappa = 0.165 \pm 0.033$ ) measured in the 99.4-99.9 % RH range using continuous-flow thermal gradient column and with the HHTDMA - based value of  $\kappa = 0.162$  reported by Suda and Petters (2016) at RH > 90%. Note that at the same water activity range the measurement uncertainty of  $\kappa$  with the HHTDMA method is  $\sim 6$  times less than that in the thermal 650 gradient column setup (0.006 vs. 0.033). As mentioned before, the optical measurements used for particles size determination (Ruehl et al., 2010; Wex et al., 2005; Suda and Petters, 2013) are subjected to limitations in accuracy resolution due to uncertainties in refractive index and the conversion from optical to physical diameter.

### 5.3.2 Activity and molal osmotic coefficients

Figure 12a shows HHTDMA-based activity coefficient of water ( $\gamma_w$ ) and glucose ( $\gamma_{Gl}$ ) in glucose 655 aqueous solution. Activity coefficient of water was calculated from Eq.(15) were  $x_w$  was obtained based on Eq.(8) and Eq.(9) as described in Sect.4.4, and water activity was derived from Eq.(6) with assumptions considered in Sect. 4.2. The activity coefficient of glucose in water solution was obtained by numerical integration of Eq. (26) (Sect. 4.4).

The bulk DRH of glucose varied in the range of 88-90 % RH (Zamora et al., 2011 and references 660 therein) that corresponds to the saturated mole fraction of glucose aqueous solution,  $x_{Gl}$  of 0.095 ( $\mu_{Gl}$  661 = 3.14 mol kg<sup>-1</sup>). Above this value, glucose particles are metastable supersaturated droplets (selected area in Fig.12a), which are present in an amorphous (semi-solid) state. Using bulk water pressure method Taylor and Rowlinson (1955) have obtained the water activity coefficient values up to  $x_w$  of 665 0.195 and fitted their data using two-suffix Margules Eq.(16) with  $A = -1.957 (\pm 0.062)$ . Figure 12a shows that up to  $x_w$  of 0.42 our HHTDMA-derived values of  $\gamma_w$  are in excellent agreement with Taylor and Rowlinson (1955) data fit indicating that simple two-suffix Margules equation with  $A = -1.957$  is also applicable for deep metastable area. Water activity coefficients obtained in this study we also compared with those reported by Suda and Petters (2013) (Fig. 12a, green line). ~~Their HTDMA-derived  $\gamma_w$  values are slightly lower than ours. At  $x_{Gl} < 0.07$  their HTDMA-derived  $\gamma_w$  values are in a good~~ 670 ~~agreement with ours (within ~0.2%), while at  $x_{Gl} > 0.07$  a systematic deviation is observed, reaching ~7% at  $x_{Gl} = 0.25$ .~~ The observed difference can be explained by the fact that Suda and Petters (2013) used assumption of volume additivity to calculate water activity coefficient. Moreover, as mentioned above, in their study no shape factor correction for the dry particles was made.

In addition, Fig.12a shows the glucose activity coefficients, which are compared to bulk 675 measurements by Miyajima et al. (1983) obtained with the isopiestic method (black symbols). One can see that our  $\ln \lambda_{Gl}$  values are in a good agreement with literature data points. For future applications, we fitted our  $\ln \lambda_{Gl}$  data (up to  $x_w = 0.42$ ) together with the Miyajima et al. (1983) bulk results using a polynomial 4th-order fit function. The obtained fitting coefficients are listed in Table 3.

Figure 12b shows HHTDMA-based molal osmotic coefficient of glucose,  $\Phi_{Gl}$  as a function of 680 water activity. The molal osmotic coefficient was calculated from Eq. (21) where  $\mu_{Gl}$  was obtained using Eq. (14). The obtained data pairs  $\Phi_{Gl}$  vs.  $a_w$  were fitted using theory relation (Eq. 23) proposed by Rudakov and Sergievski (2009) (Sect. 4.3). The best fit value of the hydration number,  $h^0$  is  $1.88 \pm 0.04$  ( $n = 75$ ;  $R^2 = 0.858$ ). That is close to  $h^0 = 1.7 \pm 0.5$  reported by Rudakov and Sergievski (2009). Our HHTDMA-based values of  $\Phi_{Gl}$  are within  $h^0 \pm 0.5$  (gray shaded area, Fig.12b). At  $a_w > 0.98$  the 685  $\Phi_{Gl}$  value is  $1.034 \pm 0.025$  (average  $\pm$  propagated uncertainty; 11 data points). This result indicates that even in diluted glucose solution, nonideality caused by hydration of glucose molecules still persists. Experimental values of  $\Phi_{Gl}$  we accompanied to those obtained by Suda and Petters (2013) (black circles, Fig.12b). In general, Suda and Petters (2013) data points are close to our results. A noticeable deviation is observed in the water activity range of 0.85 – 0.95. The main reason is that the relatively small 690 changes in the instrumental uncertainties of aerosol particle growth factors and in RH will lead to large uncertainties in the determination of their thermodynamic characteristics. Thus, for our HHTDMA system in case of glucose aerosol particles in the RH range of 90-99% the growth factor uncertainty of ~0.6% (Eq.2) gives rise the uncertainty in  $\Phi_{Gl}$  of ~3 %.

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695 **6. Summary and conclusions**

We have demonstrated the key features of newly designed HHTDMA instrument which allows measuring the particles hygroscopic growth with uncertainty of  $\sim 0.6\%$  throughout the 2 - 99.6% RH range. This accuracy was firstly achieved by combining the restructuring mode with conventional hydration/dehydration mode. The tandem of two modes allowed us to minimize uncertainties associated 700 with morphology of the initial dry particles. Secondly, both DMAs were temperature-stabilized. The temperature difference between sheath and excess flow in DMA2 is as small as  $\pm 0.015^\circ\text{C}$ , which made it possible to measure particle growth factors up to 99.6% RH. Throughout the all relative humidity range, the absolute RH uncertainty is less than 0.4%.

We have checked the effect of size dependence of the DMA2 transfer function width and sensitivity 705 of the SMPS inversion algorithm on the uncertainty in particles sizing. Our test measurements have shown that effect of transfer function broadening on the particle growth factor is negligibly small. With regard to SMPS inversion algorithm and log-normal fit used for determination of the particle mobility diameter we found that particle size resolution significantly exceeds the size of individual bins. It is possible because DMA1 selected particle are still polydisperse and a small offset voltage leads to a 710 change in the count statistics in each size bin. As a result, the fitted size spectra and modal mobility particle diameter shifts proportionally to the voltage change. Thus, in our experiments for  $\sim 100\text{ nm}$  aerosol particles we were able to maintain the required initial mobility diameter with resolution of  $\pm 0.03\text{ nm}$  by changing the voltage on the DMA1 rod by several tens millivolts.

Multiple experiments with h&d mode (pre-conditioning mode) have shown that this mode provides 715 complementary information about microstructural rearrangement processes upon aerosol particles interaction with water vapor. It allowed as quantifying envelope shape and porosity of the spray-dried ammonium sulfate and glucose aerosol particles. Changing the drying conditions, we have found that in contrast to glucose aerosol particles the water release by ammonium sulfate particles is kinetically limited most likely due to closed or partially shielded cavities. Overall, our h&d experiments showed 720 that particle envelope and porosity are not constant. Depending on drying conditions, they can vary from case to case in a wide range of particle shape factor. Therefore, for accurate growth factor determination, we recommend combining *in-situ* restructuring mode with hydration/dehydration modes. Since the restructured particles become compact, we were able to measure the thickness of the water adsorption layer on the surface of the ammonium sulfate particles before DRH. We found that water adsorption 725 occurs already at lower humidities, ranging from  $\sim 15\%$  RH. The number monolayers linearly increased from  $\sim 0$  to 3.5 for the range of 5-75 % RH and sharply increased up to  $\sim 6$  monolayers over the range of 75-79% RH.

Hydration/dehydration experiments with ammonium sulfate particles showed that experimental growth factors are in a good agreement with E-AIM model confirming that after pre-conditioning the 730 restructured particles are compact and spherical. Averaged over the range of 38 – 96 % RH, the mean deviation between measurement and model results is < 0.5 %. We also tested the RH accuracy, which can be obtained from conversion of experimental growth factors into RH using E-AIM. Due to low 735 instrumental growth factor uncertainty, we were able to measure RH above 80% with absolute accuracy no worse than 0.3 % RH. Moreover, this uncertainty decreased with RH increasing, dropping to 0.03 % at RH = 99.5 %. Thus, using ammonium sulfate growth factors as a calibration standard it was possible to eliminate RH uncertainty generated by capacitive and dew point sensors at RH above 80 %. In general, we have shown that tandem h&d (pre-conditioning) and hydration/dehydration modes, as well 740 as improved methods for measuring the RH creates the prerequisites for accurate determination of the thermodynamic parameters of aerosol particles in the wide range of RH. The effectiveness of this approach has been tested on glucose aerosol particles.

The glucose growth factors measured in the 2-99.6 % RH range are in a good agreement with literature data. At RH above 90 %, a perfect agreement between our data and those obtained by bulk methods was observed. Up to 99.6 % RH, average deviation of experimental growth factors from the full Köhler is as small as 0.7%. At water activity above 0.98, the calculated value of  $\kappa$  is  $0.160 \pm 0.006$ . 745 The HHTDMA-based activity coefficient of water and glucose in glucose aqueous solution has been obtained including metastable area up to  $x_w = 0.42$ . Both HHTDMA-derived activity coefficients are in a good agreement with those obtained by bulk methods reported in literature. We also calculated molal 750 osmotic coefficient of glucose and estimated hydration number, which is ~1.9. One should note that all thermodynamic parameters were obtained without assumption of volume additivity. Since the thermodynamic characteristics of glucose aqueous solution above bulk DRH are well defined, it can also be used as a reference standard for RH determination from experimental growth factors. It will reduce the upper limit of voltage applied to DMA2 and avoid potential discharge in the column at high RH.

Overall, our results demonstrated that the HHTDMA system described in this work allows us to 755 determine the thermodynamic characteristic of aqueous solutions with an accuracy close to that obtained by bulk methods. At the same time, an important advantage of this method is the ability to determine these characteristics for highly supersaturated solution droplets.

*Author contributions.* E.F.M. designed the study, performed the measurements, and wrote this paper. 760 S. S. Vlasenko contributed to the discussion and interpretation of the results.

*Data availability.* [Data used in this study can be made available upon request to the author.](#)

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Done

The data are available at <https://osf.io/87526/>

*Competing interests.* The authors declare that they have no conflict of interest.

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1010 **Table 1.** Microstructural rearrangement parameters for pure ammonium sulfate and glucose aerosol particles obtained in *h&d* experiment for different drying conditions (Fig. 4a and 4b).  $D_{b,i}$  and  $D_{b,h\&d,min}$  are mean  $\pm$  standard deviation of 7–10 data points; dynamic shape factor,  $\chi$ , porosity,  $\delta$ , and void fraction,  $f$  together with propagated error,  $\Delta f$  are calculated from Eq.(3), Eq.(4), and Eq.(5) respectively. r.t. is the residence time. The  $\chi$  and  $\delta$  propagated uncertainty is better than  $\pm 0.002$ .

Type of dryer	r.t. (s)	$D_{b,i}$ (nm)	$D_{b,h\&d,min}$ (nm)	$\chi$	$\delta$	$f \pm \Delta f$ (%)
Ammonium sulfate						
MD-700	27	100.26 $\pm$ 0.03	98.39 $\pm$ 0.03	1.033		
MD-700	41	100.26 $\pm$ 0.05	98.21 $\pm$ 0.03	1.037		
MD-700	54	100.26 $\pm$ 0.02	98.15 $\pm$ 0.05	1.038		
MD-700	67	100.25 $\pm$ 0.02	98.00 $\pm$ 0.05	1.040		
MD-700 + SDD	27 + 62	100.24 $\pm$ 0.03	95.32 $\pm$ 0.03	1.092	1.032	9.0 $\pm$ 0.3
		100.26 $\pm$ 0.02	95.39 $\pm$ 0.03	1.090	1.031	8.7 $\pm$ 0.3
SDD	62	100.26 $\pm$ 0.03	93.16 $\pm$ 0.04	1.137	1.056	15.1 $\pm$ 0.2
		100.26 $\pm$ 0.02	93.45 $\pm$ 0.06	1.131	1.053	14.3 $\pm$ 0.2
Glucose						
MD-700	27	100.25 $\pm$ 0.03	96.94 $\pm$ 0.03	1.060	1.034	9.5 $\pm$ 0.3

MD-700	41	100.24 $\pm$ 0.01	96.74 $\pm$ 0.03	1.064	1.036	10.2 $\pm$ 0.3
MD-700 + SDD	41 + 62	100.25 $\pm$ 0.05	96.7 $\pm$ 0.04	1.064	1.036	10.1 $\pm$ 0.3
SDD	62	100.25 $\pm$ 0.04	96.96 $\pm$ 0.04	1.060	1.034	9.5 $\pm$ 0.3

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**Table 2.** Parameters characterizing the hygroscopic properties of glucose aerosol particles: best-fit values ( $\pm$  standard errors) for the three-parameter fit ( $k_1, k_2, k_3$ ; Eq.17).  $n$  and  $R^2$  are the number of data points and the coefficient determination of the fit, respectively.

1020

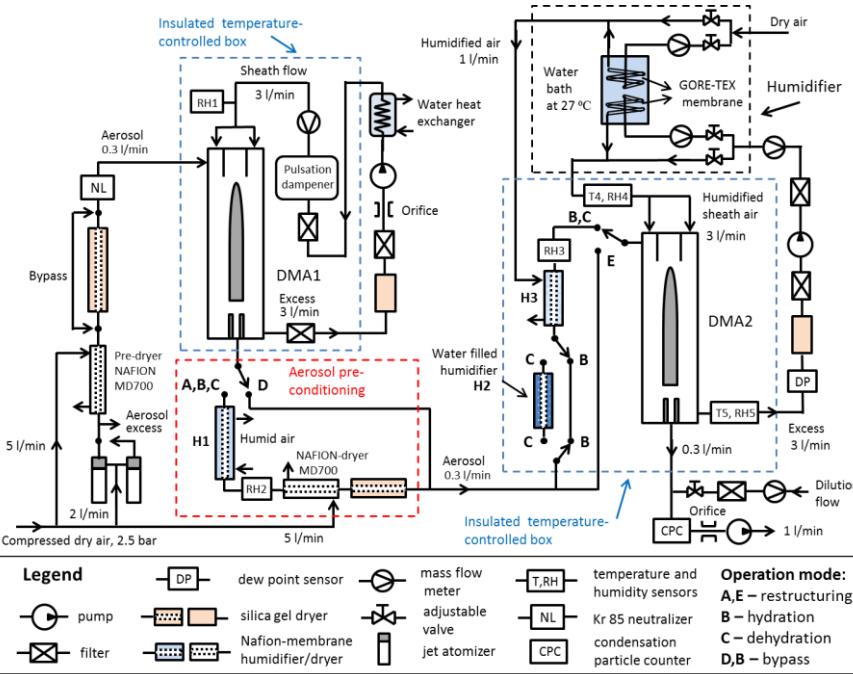
$k_1$	$k_2$	$k_3$	$R^2$	$n$	$a_w$ range
0.2629 $\pm$ 0.0272	0.05796 $\pm$ 0.0662	-0.1655 $\pm$ 0.0399	0.9994	142	0.02 - 0.98

**Table 3.** Fitted parameters ( $\pm$  standard deviation) of  $\ln\lambda_s$  as a function of mole fraction of glucose,  $x_{Gl}$  in glucose aqueous solution.  $n$  and  $R^2$  are the number of data points and the coefficient determination of the fit, respectively.

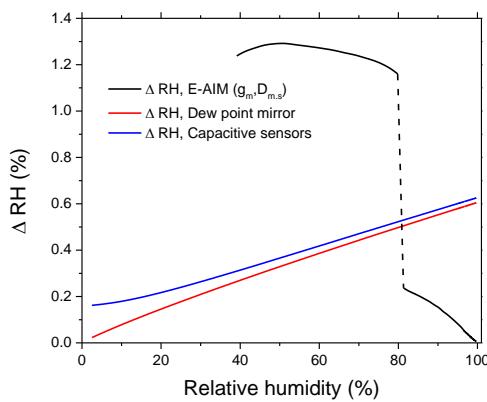
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Polynomial fit function: $\ln\gamma_{Gl} = B_0 + B_1 x_{Gl} + B_2 x_{Gl}^2 + B_3 x_{Gl}^3 + B_4 x_{Gl}^4$							
$B_0$	$B_1$	$B_2$	$B_3$	$B_4$	$n$	$R^2$	$x_w$ range
-0.0085 $\pm$ 0.0059	2.5846 $\pm$ 0.3158	17.880 $\pm$ 3.675	-79.036 $\pm$ 14.862	92.138 $\pm$ 19.152	103	0.996	0.002 - 0.42

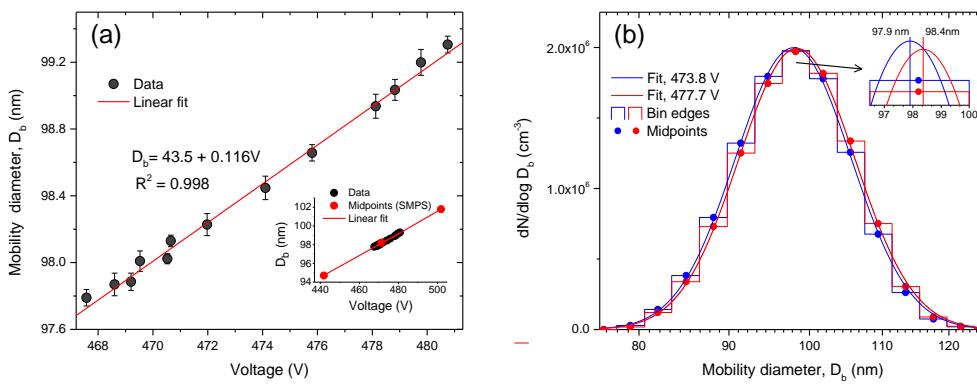
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**Fig. 1.** Schematic design of HTDMA setup: RH—RH5 – relative humidity sensors (Almemeo, FHAD 46C41A); T4, T5 – needle sensors (Pt100, 1/3, 300×1.5 mm, DOSTMANN-electronic); DP – dew point sensor (Dew Master, Edgetech Instrument, remote D-probe SC); DMA1 DMA2 – differential mobility analyzer (TSI 3081), mass flow meter – (TSI 4040), NAFION humidifier (Perma Pure; MD-110/P), jet atomizer – (3076, TSI), CPC – condensation particle counter (3772, TSI)

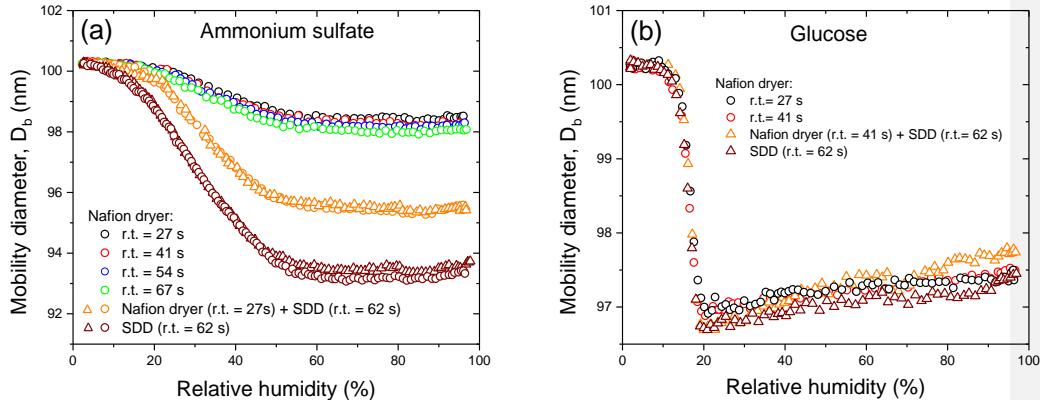


**Fig. 2.** Accuracy in RH using different methods.



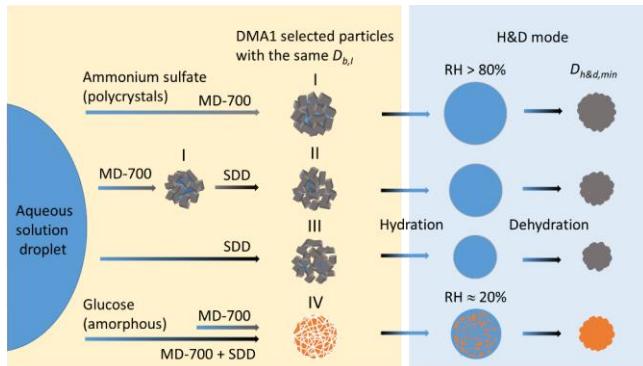
**Fig.3** Modal mobility equivalent diameters obtained by the log-normal fit of the SMPS size distribution (DMA2) as a function of the voltage applied to DMA1 center rod **(a)** and histogram together with fit curve received for two selected voltage **(b)**.

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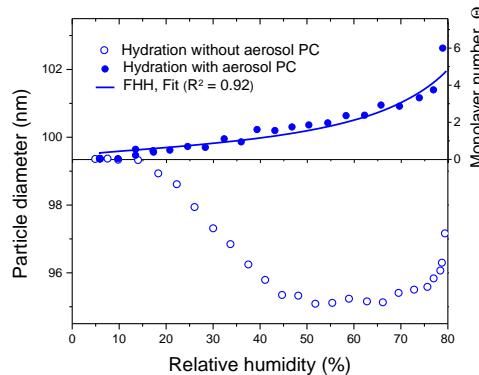


**Fig.4** Mobility equivalent diameters of ammonium sulfate **(a)** and glucose **(b)** with the initial dry mobility equivalent diameter,  $D_{b,i} = 100.3$  nm observed upon hydration & dehydration (h&d mode, RH2) depending on drying conditions. Different symbols are different experimental runs (panel **a**).

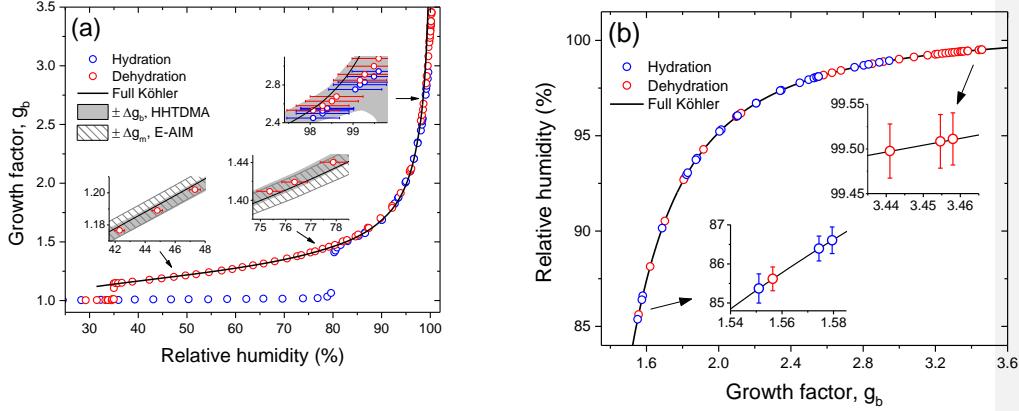
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**Fig. 5** Possible structures of polycrystalline ammonium sulfate and amorphous glucose aerosol particles depending on drying conditions: (I) agglomerate of single crystals with fully and partly shielded cavities filled with liquid; (II) and (III) polycrystalline agglomerates with open and shielded cavities, having different void to solid ratio; (IV) amorphous glucose aerosol particle in gel-like state. Other explanations are given in the text.

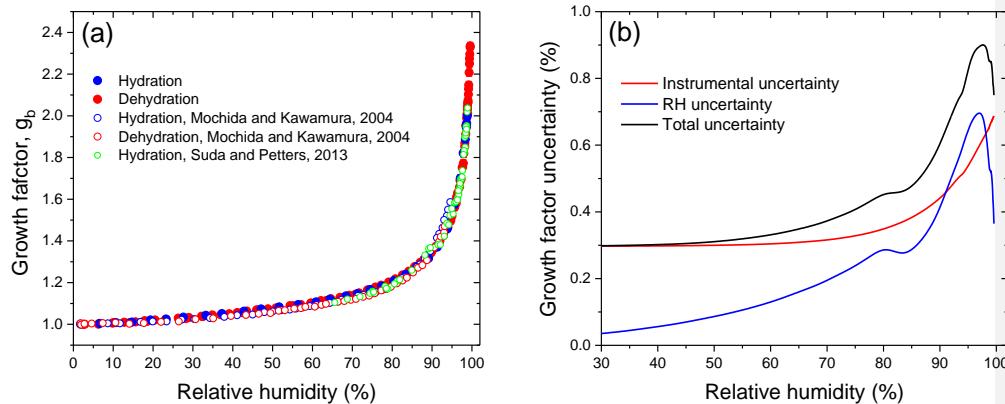


**Fig. 6** Mobility equivalent diameters of ammonium sulfate particles observed in hydration experiments with and without pre-conditioning and equivalent number of monomolecular layers.  $\Theta$  was calculated from Eq.(27) assuming that  $D_{b,h\&d,min} = D_{m,s} = 99.35 \pm 0.03$  nm, obtained with aerosol particle pre-conditioning. Line is Köhler model fit, (Eq. 6) with water activity from FHH adsorption isotherm (Eq. 28).



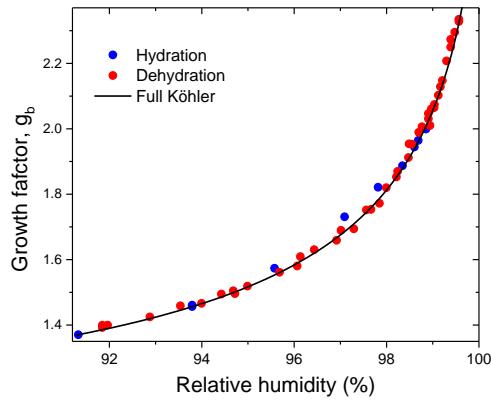
**Fig. 7.** Growth factors observed in hydration and dehydration experiments of the pre-conditioned ammonium sulfate aerosol particles with  $D_{b,h\&d,min} = 79.6$  nm as compared with full Köhler model: (a) growth factors as a function of relative humidity measured with capacitive RH probe (RH4, Fig.1); (b) RH values were obtained from E-AIM using experimental growth factors. Insets in panel (a): the gray area denotes the growth factor uncertainty obtained from Eq. (2); the shaded area corresponds to growth factor uncertainty of E-AIM below DRH obtained from EDB experimental data. Whiskers show RH uncertainty (panels a,b).

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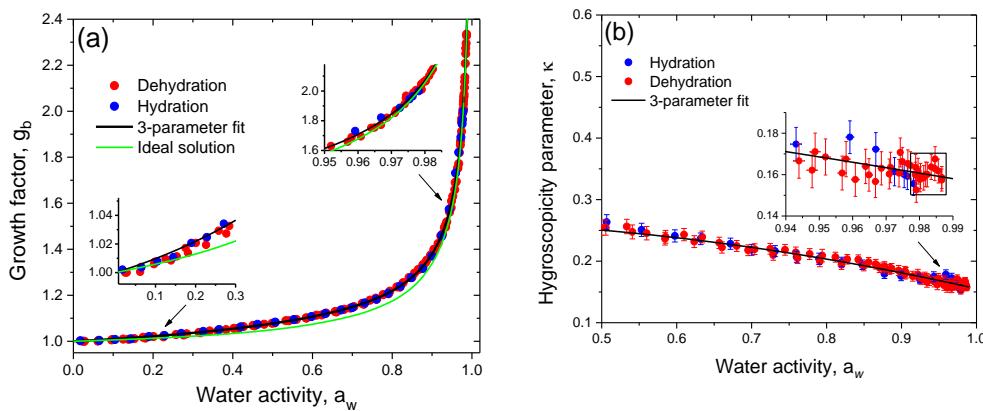
**Fig. 8.** Growth factors observed in hydration and dehydration experiments of the pre-conditioned glucose aerosol particles with  $D_{b,h\&d,min} = 99.6$  nm in comparison with literature data (a) and relative growth factor uncertainty due to instrumental and RH errors (b).

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**Fig. 9.** Growth factors observed in hydration and dehydration experiments of the pre-conditioned glucose aerosol particles with  $D_{b,h\&d,\min} = 99.6$  nm in comparison to mass equivalent growth factors calculated with full Köhler model.

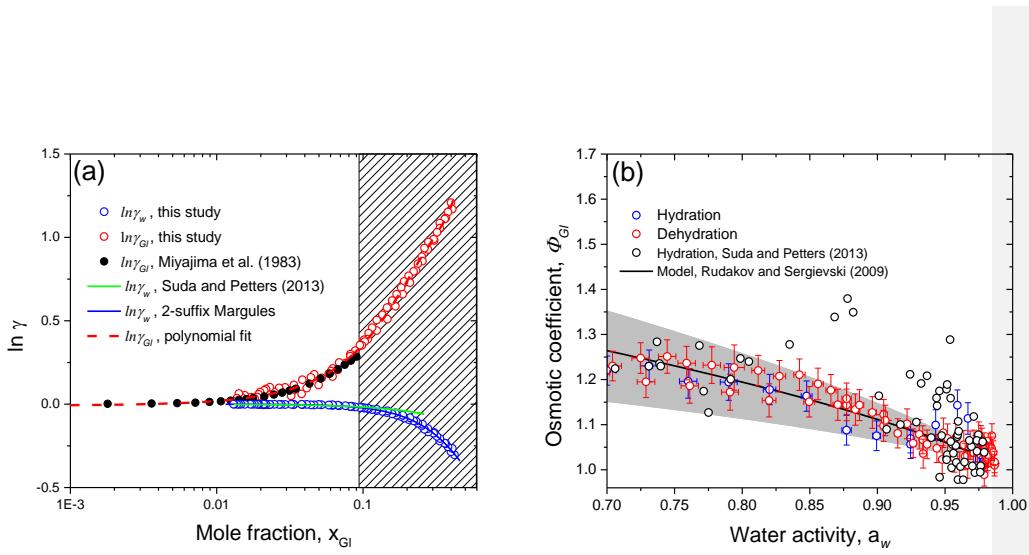
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**Fig. 10.** Growth factor (a) and hygroscopicity parameter (b) of glucose aerosol particles as a function of water activity. Black lines in panels (a) and (b) correspond to three-parameter fit using Eq.(17) and Eq.(19), respectively. Green line account for ideal solution model (a). Insets: (a) show water activity based growth factors at low and high  $a_w$  in comparison with model curves; (b) shows hygroscopicity parameter change at  $a_w$  above 0.94; data points selected by the rectangle are used to calculate the average value of dilute hygroscopicity parameter,  $\kappa$ .

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**Fig.11.** HHTDMA-based activity coefficients of water ( $\gamma_w$ ) and glucose ( $\gamma_{\text{Gl}}$ ) as a function of mole fraction (a) and molal osmotic coefficient ( $\phi_{\text{Gl}}$ ) vs. water activity (b) for glucose solution droplets in comparison with literature data. Bulk measurement of  $\gamma_{\text{Gl}}$  from Miyajima et al., (1983) – black solid (a); the data points and error bars are from HHTDMA experiment of hydration (blue circles) and dehydration (red circles) (b) ,  $\phi_{\text{Gl}}$  from Suda and Petters (2013) – black circles (b). Model lines: (a) 2-suffix Margules equation (Eq.16, with  $A = -1.957$ ) – blue solid; (b) Rudakov and Sergievski (2009) model (Eq. 23) with hydration number of  $h^0 = 1.88$  (the best fit parameter with standard error is of 0.04) – black solid. Gray shaded area denotes hydration number range with the  $h^0 + 0.5$  (top bound) and  $h^0 - 0.5$  (low bound). Red dashed fit line in panel (a) is the polynomial 4th-order fit function of  $\ln \gamma_{\text{Gl}}$  obtained in this study together with Miyajima et al. (1983) bulk measurements. The shaded rectangle in panel (a) denotes metastable area of glucose solution droplets.

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