Responses to Anonymous Referee #2

General comments:

Shen et al. present a new algorithm for the size-resolved correction of the hygroscopicity, κ considering shrinking effect caused by to multi-charge number contribution. I recommend this manuscript to be published in AMT after the following issues to be addressed and modified.

General response: Thank you very much for your review of our manuscript. Your comments were very helpful and constructive in improving this work. Below we will respond to your comments one by one. Your comments are in bold italics, and my responses are in plain text. In the end of this reply, we also attach our supplement materials.

Major comments:

- The term "shrinking effect" seems to be unfortunate, since it used for actual irregular particles restructuring in the humid conditions caused by surface or capillary forces of absorbed/adsorbed water. To avoid confusion, I recommend using another term, say "compression effect" or "displacement effect". Response: In the AMTD preprint version, we use the term 'weakening effect'. But after your comment, we think the term 'compression effect' is better and this term is being used now in the new manuscript. Thank you for your suggestion!
- 2. The shrinking function S (*i*, *v*) is not properly described in the text. Please show which expression/algorithm was used to calculate it.

Response: We don't have an analytical expression for S (i, v), but we elaborate more on the calculation procedures in the new manuscript and supplement section 2. The calculation mainly involves four steps: (1) calculate the f function as illustrated in supplement section 2; (2) for each combination of (D_p^*, v) , generate different g_0 data points and obtain the corresponding g_{DMA} from the equation 10. Then transform the GF space (g_0, g_{DMA}) to the hygroscopicity space (κ, κ_{DMA}) according to the κ -kohler theory; (3) Fit the (κ, κ_{DMA}) with a straight line across the origin and obtain the slope as the compression factor; (4) repeat the step 2-3 for different combination of (D_p^*, v) . The figure below is the algorithm procedures.



3. The multi-charge algorithm for hygroscopicity correction has not been properly tested. As a first step, I would suggest to apply it for single-component particles (100; 200, and 300 nm) with well-defined thermodynamic and hygroscopic properties, ammonium sulfate as an example. Please show the particle's growth factors change taking into account F(x, v), $\Omega(x, v, i)$ and S(i, v) and then κ initial and κ corrected as a function RH.

Response: The following is a test for our correction algorithm. The algorithm cannot ensure that the corrected particle's size-resolved hygroscopicity is fully consistent with the true values because of the measurement size resolution (detailed hygroscopicity information between measured size is lost), but the correction can improve the result to bring it closer to the true values.

If we assume a group of ammonium sulfate particles with a constant κ of 0.53. Then the HTDMA is used to scan these aerosol particles. The sample/sheath ratio of the first DMA is 1/10 and the DMA will select those negatively charged particles (DMA type from BMI). According to the following two equations:

$$N(D_p^*) = \int_0^\infty G(D_p^*, x) n(x) dx$$
$$G(D_p^*, x) = \sum_{\nu=1}^\infty F(x, \nu) \Omega(x, \nu, D_p^*)$$

the kernel function for each size set in DMA is shown below with the assumed particle number size distribution.



Fig.1: The black lines are the assumed ammonium sulfate particle's number size distribution. The blue lines are the kernel functions for the diameter set labelled in the panel.

Then we use the HTDMA to obtain the size-resolved hygroscopicity over the size of [50,100,150, 200,250, 300,400,500,600] (nm). For each diameter set D_p^* in the first DMA, it will give the corresponding measured hygroscopicity as the following equations:

$$K^*(D_p^*) = \frac{1}{N(D_p^*)} \int_0^\infty G_s(D_p^*, x) K(x) n(x) dx$$
$$G_s(D_p^*, x) = \sum_{\nu=1}^\infty F(x, \nu) \Omega(x, \nu, D_p^*) S(D_p^*, \nu)$$

Based on our calculation, we can obtain the $K^*(D_p^*)$. Then we apply our multi-charge correction algorithm in the calculated $K^*(D_p^*)$ and retrieve a corrected one. The results are listed in the figure below.

The black line is the true hygroscopicity distribution with a uniform κ of 0.53. It can be seen that the measured $K^*(D_p^*)$ deviate much from the true distributions because of multi-charge effect. The sizes of 100 and 150 nm are influenced most because the high ratio of multiply charged particles. After the correction, the hygroscopicity distribution comes very close to the true value. The large error at the size of 50 nm is due to the missing information between 50 nm and 100 nm, and the size of 50 nm is mostly affected by particles from this size range. If the measurement size resolution improves, the corrected values will come closer to the true values.



4. Due to typos and errors, the text is difficult to read.

Response: We are sorry for the difficulties we have brought to the readers and also thank you for your detailed review of this manuscript. We will try our best to find and correct all the errors, and make the new manuscript a better paper to read.

Minor comments:

- 1. *Page 1, line 30: Swietlicki et al. should be Swietlicki et al., 2008;* Response: We correct this citation in the new manuscript.
- Page 2, Line 33: (Cubison, Coe, & Gysel, 2005; Gysel, McFiggans, & Coe, 2009; Stolzenburg & McMurry, 2008; Voutilainen, Stratmann, & Kaipio, 2000). Correct citation according to AMT instruction. Response: Change made.
- 3. Line 41: "Duplissy et al. (2008) obtained ..." Note, Gysel et al., 2009 obtained the kernel function, Duplissy et al. (2008) just used it for multi-charge correction.

Response: Thank you for your reminder. We will be more careful about the citation.

- *4. Line 42 "GFs" The abbreviation is not defined.* Response: We have added the definition of GFs in this sentence.
- 5. *Page 3, Line 70, please define the scale parameter x once.* Response: We have deleted other unnecessary definition.
- *Line 74, term n(x) is not defined.*Response: Definition added to the manuscript.
- 7. Line 77, Fig, 1b. The corresponding ratio of particles carrying different charges is calculated from the PNSD using the abovementioned DMA electrical mobility and charging theory. Please specify in detail how data in Fig.1b were obtained? Show in the explicit form the F(x, v) and Ω(x, v, i), at least in Supplement. Response: We have added the detailed calculation procedures in the supplement section 1. In the text, we take DMA set size of 100 nm as an example and show that how we come to the final ratio of particles carrying different charges.
- 8. Line 80 For example, when we set 100 nm in the first DMA, more than 40% of the selected particles are multiply charged. Please double check a 40 % value. How it was obtained?

Response: As the response to the comment 7, the detailed calculation procedure is shown in the supplement. The value of 40% is reliable.

- Page 3, line 88. An illustration figure (Fig.2) was shown to explain the cause of this shrinking effect Correct the sentence. Response: Change made.
- 10. Page 4, Line 117 ...where x is the scale parameter. It was defined in page 3, line 70.

Response: This definition has been deleted in the section 3.

- 11. Line 122 So the question can be simplified as the following. Change to equation.Response: Change made.
- 12. Page 5, Line 132 One hypothetical κ distribution along with the corresponding multi-charge corrected κ distributions are shown in Fig.4. Here is discrepancy between "hypothetical κ distribution" in the text and "measured κ distribution" in the Fig.4 captions. Is it measured or hypothetical κ distribution? Response: Sorry for the ambiguity here. What we want to express is: we assume a measurement result, and then we applied our correction algorithm to this hypothetical κ distribution to find out the true κ distribution.

13. Page 6, Line 156, Eq.(12) $\mathcal{C}(\zeta, x)$ represents the correction factor caused by the shrinking effect In Eq.(6) the correction factor was defined as $\mathcal{S}(\zeta, v)$. Is it the same or new one?

Response: It is a new one. Correction factors for different parameters (here is hygroscopicity and LH fraction) are not the same.

- *14. Line 160, ... the question can be simplified into... Change to equation.* Response: Change made.
- 15. Line 167 ... distributions are also shown in Fig.4. Change to Fig.5. Response: Change made.
- 16. References Page 9, line 283

Wiedensohler, A., Lütkemeier, E., Feldpausch, M., & Helsper, C. (1986). Investigation of the bipolar charge distribution at various gas conditions. Journal of Aerosol ence, 17(3), 413-416.

Should be:

Wiedensohler, A., Lütkemeier, E., Feldpausch, M., and Helsper, C.: Investigation of the bipolar charge distribution at various gas conditions, J. Aerosol Sci., 17, 413-416, https://doi.org/10.1016/0021-8502(86)90118-7, 1986.

Please follow the AMT instruction for paper submission, especially references and citation section.

Response: we have checked again the references and citations to ensure the proper format.

Supplement for

Effects of Multi-Charge on Aerosol Hygroscopicity Measurement by HTDMA

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1. The procedures of calculating the number ratio of particles carrying different charges.

Step 1. Calculate the particle charge distribution.

The particle charge distribution at each size is based on a theoretical model developed by Wiedensohler et al. (1986). To calculate the fraction of particles carrying zero, one or two charges, use the equation below:

a _i (N)	N=-2	N=-1	N=0	N=1	N=2
a_{o}	-26.3328	-2.3197	-0.0003	-2.3484	-44.4756
a_1	35.9044	0.6175	-0.1014	0.6044	79.3772
a_{2}	-21.4608	0.6201	0.3073	0.4800	-62.8900
a_{3}	7.0867	-0.1105	-0.3372	0.0013	26.4492
$a_{_4}$	-1.3088	-0.1260	0.1023	-0.1553	-5.7480
a_{5}	0.1051	0.0297	-0.0105	0.0320	0.5049

$$f(D_p, N) = 10^{\left[\sum_{i=0}^{5} a_i(N)(\log \frac{D_p}{nm})^i\right]}$$

For the fraction of particles carrying three or more charges, use the equation below:

$$f(D_p, N) = \frac{e}{\sqrt{4\pi^2 \varepsilon_0 D_p \kappa T}} \exp \frac{-\left[N - \frac{2\pi \varepsilon_0 D_p \kappa T}{e^2} \ln(\frac{Z_{i+}}{Z_{i-}})\right]^2}{2\frac{2\pi \varepsilon_0 D_p \kappa T}{e^2}}$$

where e is the elementary charge of 1.60217733E-19 coulomb; ε_0 is the dielectric constant of 8.854187817E-12 farad/m; the D_p is the particle diameter in [m]; κ is the Boltzmann's constant of 1.380658E-23 joule/K; T is the temperature in [K]; N is the number of elementary charge units; $\frac{z_{i+}}{z_{i-}}$ is the ion mobility ratio of 0.875.

Here we present bipolar particle charge distribution with number of charges up to 4 over the size range of 10-1000 nm.



Fig.S1: Calculated number fraction of bipolar charged particles as a function of particle size. Curves decreasing in maximum charged fraction from left to right represent particles with 1 through 4 charges respectively.

Step 2: Calculate the DMA transfer function and Kernel function for each size set at DMA. In our field measurement, the DMA (BMI, Model 2100) selected those negatively charged particles. The sample/sheath ratio of 0.75/4 is used to calculate the transfer function. Then the Kernel function can be obtained from:

$$G(D_p^*, x) = \sum_{\nu=1}^{\infty} F(x, N) \Omega(x, N, D_p^*)$$

The following is an example for the DMA set size of 100 nm.



Fig.S2: The left figure is the calculated DMA transfer function for the DMA set size of 100 nm for different charges carried. The right figure is the calculated Kernel function of particles as a function of particle size. Triangle peaks from left to right represent particles with increasing number of charges.

Step 3. Calculate the (1) the total number concentration of particles that can pass through the DMA and (2) the number concentration of particles carrying v charges. In this step, particle number size distribution data is needed.

$$N(D_p^*) = \int_0^\infty G(D_p^*, x) n(x) dx$$
$$N_v(D_p^*) = \int_0^\infty G_v(D_p^*, x) n(x) dx$$

Here we present a particle number size distribution data during the relatively polluted period in our field measurement. When combined with the total kernel function or charge-resolved kernel function, we can obtain the corresponding number concentration of particles that can pass through the DMA. Fig.S3 shows an example when the DMA set size is 100 nm. It can be seen that when the accumulation mode particles increase, the doubly or triply charged particles also increase greatly. In this case, when integrated over the whole size range, the singly charged particles only constitute 55% of all the particles that can pass through the DMA.



Fig.S3: (a) The blue line represents the measured particle number size distribution. The red line represents the calculated kernel function for DMA set size of 100 nm. (b) Calculated number concentration of particles that can pass through the DMA when the DMA set diameter is 100 nm. Triangle peaks from left to right represent particles with increasing number of charges.

2. The calculation and properties of f function

In the paper, f function is defined as:

$$D_p^{\nu} = f(D_p^*, \nu)$$

It describes the physical diameter of charged particles with the known parameters of electrical mobility diameter (D_p^*) and number of charges (v).

We don't have an analytical expression for f function, but it can be calculated through two steps:

(1) Calculate the electrical mobility Z_p from D_p^* using the following equation:

$$Z_p = \frac{eC(D_p^*)}{3\pi\mu D_p^*}$$

(2) Solve the following nonlinear equation and get the best fit D_p^{ν} through the optimization method.

$$Z_p = \frac{\operatorname{ve} C(D_p^{\nu})}{3\pi\mu D_p^{\nu}} = \frac{eC(D_p^{\nu})}{3\pi\mu D_p^{\ast}}$$
$$\mathcal{V} C(D^{\nu}) = C(D^{\ast})$$

It will simplify into:

$$\frac{\nu C(D_p^{\nu})}{D_p^{\nu}} = \frac{C(D_p^*)}{D_p^*}$$

The Cunningham slip correction C can be calculated as:

$$C = 1 + Kn[\alpha + \beta \exp(\frac{-\gamma}{Kn})]$$

where $\alpha = 1.142$, $\beta = 0.558$, $\gamma = 0.999$ (Allen & Raabe, 1985). Kn is the Knudsen Number of $2\lambda/D_p$, and λ is the gas mean free path with the expression of $\lambda_r (\frac{P_r}{P_r})(\frac{T}{T_r})(\frac{1+S/T_r}{1+S/T})$. S is the Sutherland constant of 110.4 K; T is the temperature in [K] and T_r is the reference temperature in [K].

Here, we give an example of the Cunningham slip correction C with the temperature of 25 °C and pressure of 101300 Pa. $f(D_p^*, v)$ curves are also shown with 1 through 4 charges respectively. It can be seen that when v = 1, the D_p^v is equal to D_p^* . When v > 1, the D_p^v is larger than D_p^* .



Fig.S4: Calculated Cunningham slip correction and f function curve.

Reference

Wiedensohler, A., Lütkemeier, E., Feldpausch, M., and Helsper, C.: Investigation of the bipolar charge distribution at various gas conditions, J Aerosol Sci, 17, 413-416, <u>https://doi.org/10.1016/0021-8502(86)90118-7</u>, 1986.