Response to Anonymous Referee #2

We thank Anonymous Referee #2 for the review, constructive comments and suggestions for improvement of our manuscript. Detailed responses to the individual comments (including additional information and figures from the revised manuscript) are given below.

(Referee comments in *italics*, the responses in plain font)

Comments and suggestions:

Abstract: Please include 1-2 sentences early in the abstract presenting an introduction to the concept and why we want a hygroscopicity distribution. Explain why it is needed, why it is useful.

Responses and Revisions

We added a new paragraph in the abstract to explain the usefulness of the concept and some future aspects.

Page 1 line 13:

"For detailed characterization of aerosol hygroscopicity distributions, including externally mixed particles of low hygroscopicity such as freshly emitted soot, we suggest that size-resolved CCN measurements with a wide range and high resolution of water vapor supersaturation and dry particle diameter should be combined with comprehensive HTDMA measurements and size-resolved or single-particle measurements of aerosol chemical composition, including refractory components. In field and laboratory experiments, hygroscopicity distribution data from HTDMA and CCN measurements can complement mixing state information from optical, chemical and volatility-based techniques. Moreover, we propose and intend to use hygroscopicity distribution functions in model studies investigating the influence of aerosol mixing state on the formation of cloud droplets. "

Comments and suggestions:

Introduction: Out of 38 references, 21 references are self-citations (i.e. one or more of the co-authors from Su et al. is also a co-author on 21 references). It would be beneficial to include a short paragraph describing some of the recent work performed in HTDMA and CCN studies and the evaluation of kappa by research groups other than the co-author list. As a suggestion the paragraph could be located between lines 24 and 25 on page 1006.

Responses and Revisions

We included more references in the revised manuscript, e.g. in the introduction we added:

Page 2 line 47-51:

"Early and recent HTDMA studies have already presented distributions of diameter growth factors, which are also related to particle hygroscopicity, and addressed the relation to aerosol mixing state (Stolzenburg and McMurry 1988; Swietlicki et al., 2008; Kammermann et al., 2010)."

Other added references are:

Kreidenweis, S. M., Petters, M. D., and Chuang, P. Y.: Cloud particle precursors, in: Clouds in the perturbed climate system - their relationship to energy balance, atmospheric dynamics, and precipitation, edited by: Heintzenberg, J. and Charlson, R. J., MIT Press, Cambridge, 291-317, 2009.

Kuwata, M., and Y. Kondo : Dependence of size-resolved CCN spectra on the mixing state of nonvolatile cores observed in Tokyo, J. Geophys. Res., 113, D19202, doi:10.1029/2007JD009761, 2008.

Mikhailov, E., Vlasenko, S., Martin, S. T., Koop, T., and P?schl, U.: Amorphous and crystalline aerosol particles interacting with water vapor: conceptual framework and experimental evidence for restructuring, phase transitions and kinetic limitations, Atmos. Chem. Phys., 9, 9491-9522, doi:10.5194/acp-9-9491-2009, 2009.

Moore, R. H., and Nenes, A.: Scanning flow CCN analysis – method for fast measurements of ccn spectra, Aerosol Sci. Technol., 43, 1192–1207, 2009.

Moore., R. H., Nenes, A., and Medina, J.: Scanning Mobility CCN Analysis – A method for fast measurements of size resolved CCN distributions and activation kinetics, Aerosol Sci. Technol., doi:10.1080/02786820903289780, 2010.

Snider, J., Wex, H., Rose, D., Kristensson, A., Stratmann, F., Hennig, T., Henning, S., Kiselev, A., Bilde, M., Burkhart, M., Dusek, U., Frank, G., Kiendler-Scharr, A., Mentel, Th., Petters, M., and P¨oschl, U.: Intercomparison of cloud condensation nuclei and hygroscopic fraction measurements: Coated soot particles investigated during LACIS Experiment in November (LExNo), J. Geophys. Res., doi:10.1029/2009JD012618, 2010, in press.

Svenningsson, B., Bilde, M.: Relaxed step functions for evaluation of CCN counter data on size-separated aerosol particles, Aerosol Science, 39, 592–608, 2008.

Swietlicki, E., Hansson, H. C., Meri, K., Svenningsson, B., Massling, A., McFiggans, G., McMurry, P. H., Pet, T., Tunved, P., Gysel, M., Topping, D., Weingartner, E., Baltensperger, U., Rissler, J., Wiedensohler, A., and Kulmala, M.: Hygroscopic properties of submicrometer atmospheric aerosol particles measured with h-tdma instruments in various environmentsa review, Tellus B, 60, 432-469, 2008.

Comments and suggestions:

Concept and methods: I agree with the notation ambiguity discussed in the short comment by M. Gysel. I will not include detailed comments here, since M. Gysel presented a nice description outlining the issues with the notation.

Responses and Revisions

The same as in our response to Martin.

Comments and suggestions:

Page 1010, lines 17-18: It is written: "By applying Eq. (5), the normalized cumulative wet particle size distribution function N(Dw) can be converted into N*(kappa). Figure 1 shows an exemplary…". You present an equation, say you can convert one N* to another and then present Figure 1. It is not entirely clear how you go from N*(Dw) to N*(kappa). It may indeed be straightforward but a few words of explanation will make this clearer. Include a reference if needed but this should be clarified before moving onto Figure 1.*

Responses and Revisions

We added explicit equation explaining the conversion and used new symbols $F(D_w,D_d,s)$ and $H(\kappa,D_d)$ instead of N.

Page 6 line 153-154:

" … Accordingly, every HTDMA data point of $F(D_w,D_d,s)$ directly corresponds to a data point of the cumulative hygroscopicity distribution:

$$H(\kappa(D_w,D_d,s),D_d) = F(D_w,D_d,s) \quad (19)$$ "

Comments and suggestions:

Page 1010, lines 21-22 and page 1016 line 11: both of these sections discuss sizeselected aerosol data. If this data is size-selected by a DMA, there is usually a doubly charged particle mode resulting from this size-selection method. The method *of size selection as well as potential errors arising from these doubly-charged particles should be noted in the text.*

Responses and Revisions

We addressed the uncertainties introduced by the DMA and added references to the correction methods.

Page 10 line 280-284:

"The experimental uncertainties depend on various factors like instrument calibration, counting statistics, correction factors, and data inversion techniques (counting efficiency, electric charge, DMA transfer function, particle shape, etc.; Rissler et al., 2006; Rose et al., 2008; Swietlicki et al., 2008; Massling et al., 2009; Mikhailov et al., 2009; Kammermann et al., 2010; Snider et al., 2010)."

For HTDMA, page 6 line 159-162:

"The HTDMA calibration and data inversion accounted for the counting efficiency of the condensation particle counter (CPC) as well as for the transfer function of the DMA. Further details about the measurement campaign, techniques and conditions are given by Massling et al. (2009)."

For CCN, page 14 line 402-406:

"The size-resolved CCN measurements were performed following method II ("D_d scan" at constant S), and the data were recorded and processed as detailed by Rose et al. (2010a), except that the DMA transfer function correction was not applied, because it is based on the assumption of perfect internal mixing (Sect. 2.3.1.3 in Rose et al., 2008)."

Comments and suggestions:

Page 1011, lines 1-8: This section could be reworded so that it is clearer. Soon after Figure 1 is introduced, you could include another sentence explaining in a general sense what this figure tells us about mixing state. When I look at the graph, what general features am I looking for to tell me something about the mixing state? After that, go into the details with the examples that are written (i.e. that a small percentage may be externally mixed and that there may be a lognormal mode of sulfate-organic-soot mixtures). A simple sentence explanation would definitely help with the understanding. You could also explain how other types of mixtures might look different than this graph, if this is known. Lastly, please explain how the steep increase at kappa=0.5 tells us that it's lognormal, even if it seems obvious.

Responses and Revisions

Accordingly to the referee's suggestion, we addressed Figure 1 in more details and gave the coefficient of determination R^2 as an indicator for the lognormal distribution.

Page 6 line 163-172:

"The curves in Fig. 1 indicate a bimodal hygroscopicity distribution for both 80 nm and 150 nm particles. The values of $H(\kappa, D_d)$ at the lower end of the distribution curves are ~0.2, implying that ~20% of the mono-disperse particles have κ values < 0.01. These particles are most likely externally mixed soot particles freshly emitted from strong local combustion sources, which are characteristic for polluted air in Chinese megacity regions (e.g., Garland et al., 2008; Cheng et al., 2009; Garland et al., 2009; Massling et al., 2009; Wehner et al., 2009; Rose et al., 2010a,b,c). The steep increase of $H(\kappa, D_d)$ around $\kappa \sim 0.5$ indicates a lognormal mode in the hygroscopicity distribution (lognormal fits yield R^2 of 0.99), which can be tentatively explained by internally mixed particles consisting of varying amounts of sulfates, nitrates, organics and aged soot (Massling et al., 2009; Wiedensohler et al., 2009; Rose et al., 2010a,b,c)."

Comments and suggestions:

Page 1016, lines 16-17: The comparison between figure 8 and figure 5 is difficult to see. Please add further explanation. Or do you perhaps mean figure 6 rather than figure 5?

Responses and Revisions

Yes, it is hard to see. So in the revised manuscript, we compared the measured contour plots with the Case C contour plots.

Page 15 line 440-443:

"Interpolation between the PDFs observed at different supersaturations yields an approximate representation of the distribution of the particle mode with $\kappa \geqslant \kappa_{ml}$ in the D_d–κ plane as shown in Fig. 9a. Similar to the more hygroscopic mode 1 in the model scenario Case C (Fig. 4b), the modal κ value tends to increase with D_d."

Comments and suggestions:

Page 1010, lines 18-23 and page 1016, lines 11-14: you mention a field campaign in Beijing. A separate paragraph or very short section outlining the field campaign *would be useful. You could make this field campaign section "Section 2" and shift all other sections down, as a suggestion. In this section, include the name of the campaign, where and when it occurred, the main aerosol sources and which instruments are used in this work (including size-selection methods). Please include here the list of references already published about this campaign, indicating there are more details contained in that work. Then on page 1010 and 1016, simply refer to this section. As an additional point, on page 1011 lines 5-6, there is a list of 6 references for "externally mixed soot particles", this list of references could be moved to this new short field campaign section and simplified on page 1011 line 5-6 by referring to the new field campaign section.*

Responses and Revisions

We would like to thank the referee for the nice suggestion. The problem is that we also included two other campaigns as application examples in the revised version. These two campaigns are only briefly addressed since the data were already published. By making a campaign session, these two campaigns would also be included, making the manuscript more like a campaign paper which might dilute our main purpose. So we only added references to these campaigns without introducing a new session.

Comments and suggestions:

Page 1026, Figure 1: Since this is a one-day average, please include error bars or indicate what the standard deviation was. How much variation in these measurements occurred over that day? How many measurements are in this average?

Page 1032, Figure 7: When you average CCN spectra over the entire campaign, does this mean that the spectra did not change much throughout the campaign? How many measurements are in this average? What time frame is averaged over? Did you not see differences with wind direction, or diurnal patterns? Consider including error bars or indicate the standard deviation, demonstrating that it did not change significantly over the averaging period. Also consider indicating an error bar on at least one of the lines in Figure 8.

Responses and Revisions

We understand the concerns of the referee, whether such distribution is often observed or just by incidence. So we included the variation (in the form of standard deviation) of measurements over the entire campaigns as shown in Fig. 7. Each mean value data point is averaged over ~300 individual measurement covering all measurement time periods. Note that the experimental uncertainties (<10%, Rose et al., 2010a) were smaller than the temporal variability of the measurement data as indicated by the error bars.

We tried to include error bars for H(κ,D_d) then it became so tightly packed and overlapped that afterwards it was not so clear. So we didn't add similar error bars in Fig.1 and Fig.8.

Details discussion and scenario analysis about the campaigns would be interesting but it would go beyond the focus of this study. However, we are happy to make such following studies.

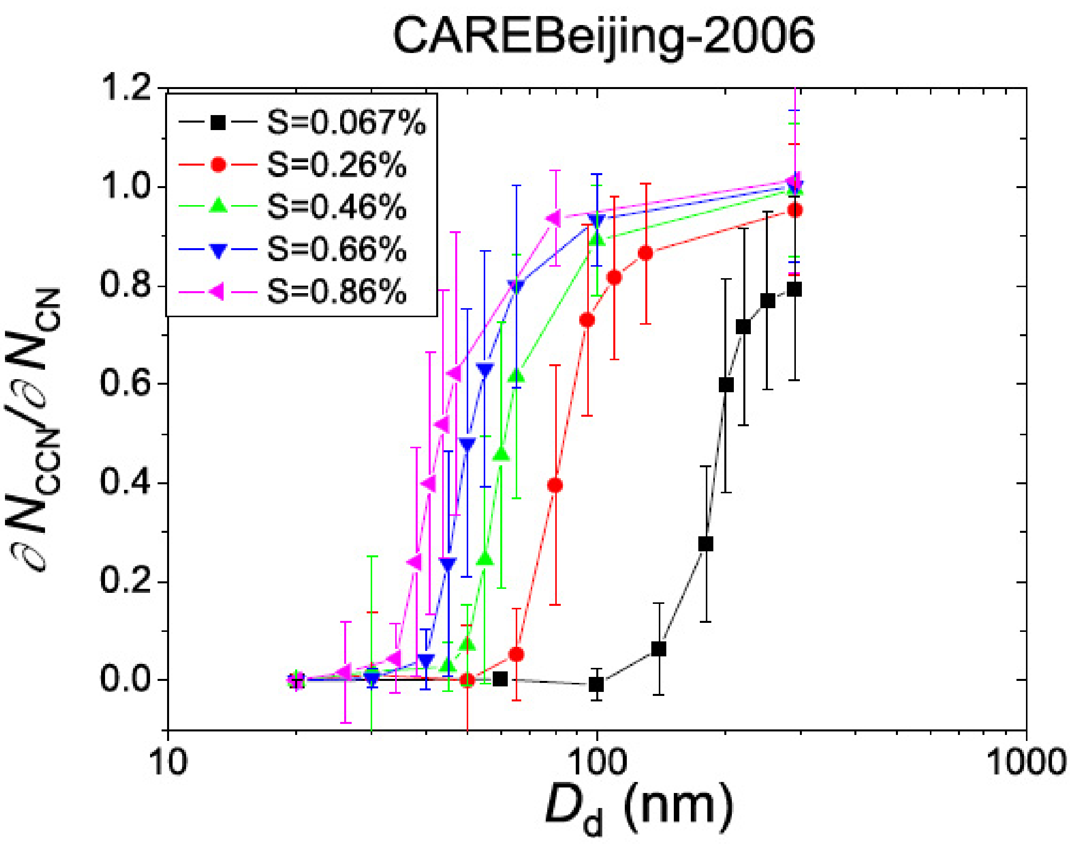

Fig. 7. Average CCN efficiency spectra for the CAREBeijing-2006 campaign (12 August to 8 September 2006, Yufa, Beijing, China). The data points and error bars represent arithmetic mean values ± one standard deviation. Note that the experimental uncertainties (< 10%, Rose et al., 2010a) were smaller than the temporal variability of the measurement data as indicated by the error bars.

Comments and suggestions:

Page 1006, line 23: If you use the word "fitting" here, it seems like you might need *further explanation in the introduction, such as what is being fit to what. This is discussed later in the manuscript so I would suggest changing "by fitting" to "from".*

Responses and Revisions

Yes, we changed it to 'from':

Page 2 line 28-29

"The values of κ can be determined experimentally from hygroscopicity tandem differential mobility analyzer (HTDMA) and CCN measurement data."

Comments and suggestions:

Page 1007, line 13 and page 1020, line 3: "Krejci et al., 2004" is 2005 in the reference list. Please fix this discrepancy.

Responses and Revisions

It is Krejci et al., 2005. Corrected.

Comments and suggestions:

Page 1008, lines 1-2: Petters et al. (2009a) do not imply combustion aerosols are kappa=0.01; there is only a small percentage that have kappas that low (this was the lowest kappa measured). This sentence implies that "aerosol combustion products have kappa=0.01". Please reword this, perhaps "For atmospheric aerosols, the range of kappa typically varies from as low as 0.01 for combustion aerosol particles…:". Also, insoluble aerosols may have kappa values very close to zero.

Responses and Revisions

We took this suggestion and use the word " … some combustion aerosol particles …" instead:

Page 3 line 61-63:

"For atmospheric aerosols, the range of κ typically varies from as low as ∼0.01 for some combustion aerosol particles up to ∼1 for sea-salt particles"

Comments and suggestions:

Page 1008, lines 2-3: Since Petters and Kreidenweis (2007) was the first paper to suggest values of kappa, please include this reference here.

Responses and Revisions

Added.

Comments and suggestions:

Page 1008, line 8: change the comma at the end of this line to a colon.

Responses and Revisions

The definition has been reformulated as:

Page 3 line 66-70:

"For particles with a dry diameter of D_d, i.e., within an infinitesimal size range of D_d to D_d+dD_d, the fractional cumulative distribution function (CDF) of hygroscopicity, H(κ,Dd) is defined as the number fraction of particles having a hygroscopicity parameter smaller than κ. In other words, $H(\kappa,D_d)$ is the number concentration of particles having a hygroscopicity parameter smaller than κ divided by the total number concentration of particles in the size range [D_d, D_d+dD_d]."

Comments and suggestions:

Page 1007, line 19: the factor, i, is not the "van not Hoff factor", but "van't Hoff factor".

Responses and Revisions

Corrected

Comments and suggestions:

Page 1011, equation (7): consider referencing Petters and Kreidenweis (2007) for this equation.

Responses and Revisions

Added

Comments and suggestions:

Page 1013, lines 17-18: remove semi-colon or bracket here "...particle shape, etc.; (Rose…". If you remove the semi-colon, close the bracket at the start of line 17.

Responses and Revisions

Corrected as:

Page 10 line 282-284:

"(counting efficiency, electric charge, DMA transfer function, particle shape, etc.; Rissler et al., 2006; Rose et al., 2008 ; Swietlicki et al., 2008; Massling et al., 2009; Mikhailov et al., 2009; Kammermannet al., 2010; Snider et al., 2010)."

Comments and suggestions:

Page 1013, line 22: "Petters and Kreidenweis, 2008" is not in the reference list.

Responses and Revisions

It is the paper in 2007. Corrected.

Comments and suggestions:

Page 1014, lines 11-12: change to "Three idealized distributions of: : :" or "Three hypothetical distributions of…"

Responses and Revisions

Changed to hypotheical.

Comments and suggestions:

Page 1015, lines 8-9: By referring to "several field measurements", it implies "several field campaigns" but I believe what is intended here is that it was several measurements during one field campaign. Please specify the location of these "several field measurements" and consider slight rewording, such as simply "several measurements during a field campaign in China" as an example. Since it seems Rose et al. 2008b may not be published in ACP, do not hesitate to add a few sentences of description from that study as you see fit.

Responses and Revisions

We included two other published campaign results into this paper:

Page 15 line 444-449:

"Besides the CAREBeijing-2006 campaign, the same approach was also successfully applied to other data sets. For example, Fig. 9b shows a similar PDF of particle hygroscopicity obtained from size-resolved CCN measurements in polluted megacity air and biomass burning smoke near Guangzhou, China (PRD2006 campaign, 1-30 July 2006; Rose et al., 2010a); and Fig. 9c illustrates a PDF of particle hygroscopicity for pristine rainforest air measured in Brazil (AMAZE-08, 14 Feb - 12 Mar 2008; Gunthe et al., 2009)."

Comments and suggestions:

Page 1016, line 21: spelling mistake in the word "hygroscopicity"

Responses and Revisions

Corrected.

Comments and suggestions:

End of Section 4 or in the conclusions: please add one sentence stating that this analysis is only performed for one study in a polluted environment. Mention that future work is needed to verify this technique with other data such as from marine and rural locations.

Responses and Revisions

In the discussion, we added another data analysis of rainforest data. In the conclusion we made corresponding revisions:

Page 16 line 479 – 481:

"(3) Lognormal distribution functions were found to be suitable for approximately describing the hygroscopicity distribution of aerosols in polluted megacity air as well as in pristine rainforest air as determined by size-resolved CCN measurements."

Comments and suggestions:

Page 1020, line 28-31: please move this reference to the next page, page 1021, line 12.

Responses and Revisions

Done.

Comments and suggestions:

Page 1021, line 10: please label this reference as "2009b"

Responses and Revisions

Labeled

Comments and suggestions:

Page 1025, Table 2: please refer to this table in the text somewhere, such as page 1008 (where the concepts are first introduced) or put this table as an appendix.

Responses and Revisions

We refer to the two tables in the text:

Page 15 line 463-464:

"…for acronyms and symbols, refer to Table. 3 and 4)"

Comments and suggestions:

Page 1031: It should be mentioned in the caption somehow that the 3 red lines all lie on the same line (as does the 3 green lines).

Responses and Revisions

Added.

Page 30 figure caption:

"The three blue (or green) lines at different S converge into a single curve."