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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Technical Note: Hygroscopicity distribution concept for measurement data analysis and modeling of aerosol particle hygroscopicity and CCN activity" *by* H. Su et al.

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This study makes a relevant contribution concerning a useful way of describing aerosol mixing state with respect to hygroscopic growth and CCN activity. Presenting mixing state resolved HTDMA or CCNC measurements as cumulative distribution functions (CDF) or equivalently probability density functions (PDF) could make results reported by different research groups much better comparable than often the case in previous studies. Bearing this in mind it is important that the formalism used here is unambiguous, complete and as general and clear as possible. Below I provide some input which

might help making this manuscript an even better and more general technical reference for future work.

1. The concept of describing the results of monodisperse CCNC measurements in the form of hygroscopicity distributions is certainly not yet wide spread and it may possibly be called new. However, this is definitely not true for hygroscopicity distributions obtained from HTDMA measurements. Stolzenburg and McMurry (1988) introduced the concept of describing inverted HTDMA measurements as a normal distribution of growth factors with their TDMAinv algorithm. Adapted versions of the TDMAinv algorithm, which describe the growth factor PDF (GF-PDF) as a superposition of multiple Gaussian distributions, have been used by many groups. Recently Gysel et al. (2009) have developed an algorithm which inverts HTDMA data and describes the GF-PDF as a piecewise linear function. The code of this algorithm also contains a function to convert a GF-PDF into a κ-PDF and it is available on the web (http://people.web.psi.ch/gysel/restricted/). In 2008/2009 HTDMA measurements have been made during a whole year at several sites across Europe as part of the EU-funded project EUCAARI. The inverted GF-PDF data of these studies are available in the form of GF-PDFs on NILU's EBAS database. Kammermann et al. (2010) showed in a hygroscopicity-CCN closure study how such GF-PDF data can be used to consider the size-resolved particle mixing state for CCN predictions. Equation (6) of this manuscript is essentially equal to equation (2) in Kammermann et al. (2010), except for describing the mixing state in κ- instead of GF-space.
2. The concept of reporting mixing state resolved HTDMA or CCNC data as κ distributions is generally applicable for any kind of mixing state found in the atmosphere. Unfortunately the theoretical concept remains confined to bimodal lognormal κ distributions as the most complex example explicitly given in this study. Bimodal lognormal κ distributions may often be sufficient to describe the properties of atmospheric aerosols but there are certainly many cases with more com-

plex κ distributions. What about the example given in Fig. 1, is it possible to represent it accurately with a bimodal lognormal distribution? How would you calculate the mean κ for these examples? In order to make this paper a complete and general reference for future studies I encourage the authors to provide the basic equations for deriving integral parameters such as (geometric) mean κ, (geometric) standard deviation, etc. from a whole κ distribution of any shape as well as for sub-ranges of the κ distribution (possibly in an appendix). The latter may for example be of interest in the case of distinct modes. Equivalent equations for GF-PDFs instead of κ-PDFs are given in appendix C of Gysel et al. (2009). Direct integration of (interpolated) κ distributions can make your life much easier when it comes to determining mean κ values of many individual distributions of a large HTDMA or CCNC data set. The detour through fitting multimodal (log-)normal distributions can be very tedious work.

3. The authors use both the cumulative hygroscopicity distribution, $N(\kappa)$, and the normalized cumulative hygroscopicity distribution, $n(\kappa)$ throughout their manuscript. I recommend that the unnormalised forms of cumulative distribution function (CDF) and probability distribution function (PDF) are completely avoided, and that only the normalized forms of CDFs and PDFs are used. Furthermore hygroscopicity distribution data, be it from HTDMA or from CCNC measurements, should always be reported in the normalised form (information on the total number of measured particle counts can always be separately added). Reasons for my strong opinion are:

   - A HTDMA provides only information on the normalised hygroscopicity distribution. Additional effort such as an extra CPC behind the first DMA, a parallel SMPS, or a very accurate characterisation of TDMA kernel (including losses in the dryer and humidifier) would be required to infer the correct factor for obtaining the unnormalized hygroscopicity distribution from the normalised form. Actually, this fact is withheld in the statement "Then a

second DMA is used to measure the size distribution of the equilibrated wet particles, $n(D_w)$ and to calculate the cumulative wet particle size distribution function, $N(D_w)$." made on p. 1010, line 4.

   - A priori the CCNC delivers via the monodisperse activation spectra the normalised form of the hygroscopicity distribution. In this case it is possible to infer the correct absolute values of the unnormalised form from the CPC data. However, it is much easier to get rid of concentration units immediately by directly using activated fractions for inferring the hygroscopicity distribution functions.
   - Hygroscopicity distributions are an intensive quantity. Therefore it is natural to use the normalised form of the hygroscopicity distributions. Absolute concentration values become only relevant, when it comes to calculating total CCN number concentrations from size dependent hygroscopicity distribution data from a HTDMA or CCNC combined with size distribution data from an SMPS. For this calculation, it is natural to have the information on absolute particle concentrations in the CN number size distribution (an extensive property), while using the normalised form of the hygroscopicity distribution to describe the mixing state (an intensive property). See also main item 4 for my request to provide the equations for this calculation.
   - Reporting unnormalised hygroscopicity distributions with absolute concentration values is very susceptible to errors because units are often ambiguous (see main item 7 for an example from within this manuscript). A typical error is a factor of ln(10) in absolute values (from using ln instead of log). The authors actually state that "we apply the same terminology and formalisms as used by Seinfeld and Pandis (2006)." However, the latter uses ln, whereas log is used in this study.

4. For completeness I suggest that equations are added, which describe how the total CCN concentration at a given SS can be obtained from measured number

size distribution data (SMPS) combined with a complete set of size-resolved κ distribution data (HTDMA or CCNC). These equations are readily obtained by adapting equations (2) and (3) from Kammermann et al. (2010) (i.e. replace GF-PDF by κ-PDF, GF_{crit} by κ_{crit}, etc.).

5. In general, and especially for the above request it is necessary to explicitly indicate which parameters are size dependent, i.e. always write $N_{CCN}(D_p)$, $N_{CN}(D_p)$ $\kappa_{cri}(D_p)$, etc. (SS dependence may also be added explicitly). This may seem tedious and an unnecessary complication of the equations. However, it is to be remembered that the dependencies of parameters on other variables is by far not always obvious for those, who have not derived the equation on their own. Omitting these dependencies can easily lead to errors if such incomplete equations are used by other groups in their studies.

6. The notation is ambiguous: "n" is used for both $n(\kappa)$ and $n(D_w)$, while $n(D_w) \neq n(\kappa(D_w))$. The same applies to $N(\kappa)$ and $N(D_w)$.

7. The units of N_{CN} are not unambiguously defined. It can be concluded from equations 3 and 6 that N_{CN} is meant to be $N_{CN}=\hat{n}_{CN}^{log}(D_p)=\frac{d\hat{N}_{CN}}{dlogDp}(D_p)$, where $\hat{N}_{CN}$ is the cumulative CN number size distribution, i.e. $\hat{N}_{CN}(D_p^*)$ is the total number concentration of particles with diameter smaller than D_p^*, and $\frac{d\hat{N}_{CN}}{dlogDp}(D_p)$ is one common way of describing particle number size distributions. The same is true for the units of N_{CCN}. The definition of N_{CCN} and N_{CN} given in Table 2 is definitely too sloppy: "The number concentration of CCN (CN) in one size bin". For an experimentalist it would be much more natural to interpret this definition as "CCN (CN) number concentration measured with the CCNC (CPC) behind the DMA", which also has the unit of an inverse volume, as indicated in Table 2 for N_{CCN} and N_{CN}. It is very easy to show that this interpretation is different from the correct one: N_{CCN} and N_{CN} would then become dependent on the flow ratio set in the DMA. Thereby equation 6 would become inconsistent because the far

left and far right part would change with changing flow ratio, while the centre part remains constant.

8. I suggest to use slightly different notation in order to make things unambiguous and closer to common notation.
   - Use $N_{CN}(D_p)$ and $N_{CCN}(D_p)$ for the cumulative number size distributions of CN and CCN, respectively.
   - Use $n_{CN}^{log}(D_p):=\frac{N_{CN}}{dlogDp}(D_p)$ and $n_{CCN}^{log}(D_p):=\frac{N_{CCN}}{dlogDp}(D_p)$ for the number size distribution of CN and CCN, respectively.
   - Use m_{CN} and m_{CCN} for the number concentration of CN and CCN, respectively, measured behind the DMA during a monodisperse CCN measurement. You may think of a better symbol than m but I do not recommend to use N, because the latter is commonly used for the cumulative size distribution function.
   - Use $a_F(SS, D_p)=m_{CCN}(SS, D_p)/m_{CN}(SS, D_p)$ for the activated fraction.
   - Use $c(\kappa)$ for the normalised hygroscopicity distribution. You may think of a better symbol than c but I do not recommend to use n^*. "n" is commonly used for number related extensive properties, whereas the hygroscopicity PDF is an intensive property.

9. It should be briefly mentioned with suitable reference to existing literature that multiple charges are always a potential issue for monodisperse measurements and how this can be addressed. Furthermore, is it possible to state whether either the D-scan or the S-scan mode is to be preferred when it comes to correction of multiple charge effects?

10. It should be emphasized that raw GF distributions measured by a HTDMA must be inverted in order to obtain a valid GF-PDF or κ-PDF. The least thing to be done with the raw HTDMA data is to correct for the growth factor dependent detection

probability. Otherwise the κ-PDFs derived from HTDMA data will be systematically biased towards the particles with higher κ-values. Statements such as "From Hygroscopicity Tandem Differential Mobility Analyzer (HTDMA) measurement data, N(κ) can be directly derived by solving the κ-K öhler model equation." should be corrected accordingly (see abstract, section 2.2, etc.).

11. State of the art approaches for acquiring D-scan and S-scan data with a CCNC should be referenced (e.g. Moore and Nenes, 2009; Nenes et al., 2010).

References

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