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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Aerosol hygroscopic growth parameterization based on a solute specific coefficient" *by* S. Metzger et al.

S. Metzger et al.

swen.metzger@mpic.de

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Reply to S. Kreidenweis (Referee)

We thank S. Kreidenweis for the constructive and helpful review.

We hope to have clarified the issues raised and satisfactorily addressed all comments with the point-to-point reply below. The suggested corrections and additions will be included in the revised manuscript.

The authors present a parameterization of aerosol water contents that can be applied to either compute the water activities of bulk solutions or, with additional terms in the equations, be used to compute water contents as a function of particle dry diameter. The parameterizations are potentially useful if they can be shown to be more accurate than existing formulations, while remaining computationally efficient.

The ν_i method is a single parameter method that is more accurate than the existing one, as shown by your Addendum and our figures 3 and 4, at least for concentrated sodium salt (NaCl) solutions. Using our complete equation (17b) this is also the case for ammonium salts (and others). It is thus the first time that a single parameter method can be used for both single and multi-charged salt-solutes in modeling the a_w from the compound's RHD until to its critical supersaturation S_c. Note that not only Eq.(17c) is a single parameter model, also Eq. (17a,b,d) only depend on ν_i. A and B and K_e depend only on the solute molality μ_s and ν_i. Equations (17a-d) provide a relation between RH and μ_s, where either RH or μ_s is regarded as the variable. Furthermore, Eqs. (17a-d) depend on the single parameter ν_i, which is determined at the point of deliquescence and afterwards kept constant over the RH-range.

In the following, I will address only one aspect of the presented work, namely the parameterization of bulk water activity as this comparison is more straightforward than those involving the Kelvin term, which depends in turn on the choice of dry diameter. The relevant equation for this special case is equation 17c, which truly is a single-parameter equation.

As noted above, Eqs. (17a,b,c,d) are single parameter models.

1. *The applicability of the PK2007 parameterization below water saturation (also evaluated, as done here, by comparing with the AIM model) was explored by*

Kreidenweis et al. (2008) [Kreidenweis, S.M., Petters, M.D., and DeMott, P.J., Single parameter estimates of aerosol water content, Environ. Res. Lett., 3, 035002, doi:10.1088/1748- 9326/3/3/035002, 2008; the authors should add this article to their references as it is directly relevant to this paper].

We agree that this article is directly relevant to the paper. We will add it to our references.

2. *SPD2008 showed that appropriate choices of kappa could generally represent the subsaturated aerosol water contents within 20%, except for sodium salts. For the sodium salts studied, the (a_w/(1-a_w)) function simply does not well represent the actual functional dependency. Thus I was particularly interested in the application of the proposed parameterization to NaCl.*

   We agree, sodium salts can not well represented by a_w/(1-a_w)) function, if only a linear correction factor is used.

3. *In the Addendum to this review I show a comparison between the present parameteri- zation, using Equation 17c and the recommended parameters for NaCl and ammonium sulfate, and the PK2007 formula using the kappa values recommended in SPD2008. Following SPD2008, the comparisons are shown in terms of the volume of water per volume of dry solute, since accurate water contents are of interest. The authors' parameterization does a nice job of representing the water contents for NaCl, much better than PK2007, and the fit for ammonium sulfate is also very good and similar to PK2007 over a wide range of water activities.*

   Thank you. As stated in your Addendum, the advantage of the ν_i formulation is that the water activity function is raised to a power (of the type xA^x), whereas the κ formulation scales linearly (of the type xA).

4. *This comparison thus demonstrates the potential utility of the new single-parameter equation (17c) in modeling water contents of atmospheric aerosol.*

   We agree but would like to add that our more complete Eq. (17d) is superior to Eq. (17c). Both are single-parameter equations, i.e. ν_i, where either RH or μ_s are treated as variable. Note that the B_{98} term is computed once ν_i is specified.

5. *I would recommend that the authors remove some of the superfluous review material at the beginning of their chapter, and present the form and results of the (bulk solution) water activity fits in a more straightforward way so they can be appreciated by a wider audience. In the present form of the manuscript it is very difficult to understand the magnitude of the differences between the various formulas used to create the HGF figures.*

   We will make this more clear in the revision and remove superfluous text.

6. *My second comment concerns the other equations presented for computing water contents (17a, 17b, 17d). If I understand correctly, in order to compute the A and B parameters, one needs not only the solute-dependent "single parameter" ν_i, but an additional piece of information that is stored for the solute under question, for example the value of molality at saturation. Thus all of the remaining equations become multi-parameter, and not single-parameter, fits; this is seen explicitly in 17d, where a new parameter B_{98} is introduced.*

   As noted above Eqs. (17a-d) provide a relation between RH and μ_s depending on one parameter ν_i, i.e. they are single-parameter equations. This can be clearly seen from equation (16a), which is just the rearrangement of the most general equation (17b). The terms A (Eq.18), B (Eq.19) are functions of μ_s with the parameter ν_i. B_{98} (Eq.20) is more simple and just a expression of the parameter ν_i. The Kelvin term K_e (Eqs.1,2) is a function of μ_s. The equations 17(a,c,d) can be seen as simplifications of the general expression (17b). Neglecting the the Kelvin effect ($K_e = 1$) leads to equation 17a. Neglecting the Kelvin effect and restricting to applications RH $<$ 98% allows one to evaluate equation 17d ($K_e = 1$, B=B_{98}, $A = 1$). Further restrictions of the RH range $<$ 95% leads to the most simple form, equation 17c ($K_e = 1$, $B = 0$, $A = 1$).

The parameter ν_i is determined from measured RHD and $\mu_{s,sat}$ with Eq. (16b), which equals Eq. (16a) for RH=RHD, μ_s=$\mu_{s,sat}$, which is the rearranged Eq. (17b). Once the parameter ν_i is determined at this point, it stays constant for the entirely range of RH and μ_s. Of course the value of ν_i depends on the choice of A, B and K_e, which have to be selected according to the application of EQSAM4 (RH range, Kelvin effect).

So for example for model applications restricted to RH $<$ 98% and ignoring the Kelvin effect, one would choose $A = 1$, $B = B_{98}$, $K_e = 1$, i.e. Eq. (17d). The parameter ν_i would be determined from Eq. (17d) (RH=RHD, μ_s=$\mu_{s,sat}$) or equivalently from equation 16b with the above choices for A, B and K_e. The now determined parameter ν_i can be used to calculate the RH-μ_s curve for RHD$<$RH$<$98% with Eq. (17d).

Note that Eq. (17d), which depends on the additional B_{98} term obtained by Eq. (20), only depends on ν_i. Thus, inserting Eq. (20) in Eq. (17d) yields a single-parameter equation:

$$\mu_s = \mu_s^o \cdot \left(\left[\frac{1}{\nu_i \cdot \mu_s^o \cdot M_w} \cdot \left(\frac{1}{RH} - 1 \right) \right]^{\frac{1}{\nu_i}} - 10^{\left[\frac{2}{\nu_i} - 2 \right]} \right) \qquad (17d)$$

The same holds for the complete equation (17b) which parameterizes the Köhler-curve. For a given dry radius the molality can be expressed as a function of wet radius (D_{wet}), Eq. 2. So A, B and K_e become functions of D_{wet} (instead of μ_s) with the single parameter ν_i. Again ν_i is determined at the point of deliquescence and kept constant when equation 17b (or its rearrangement 16a) is used to calculate the complete Köhler-curve (Fig. 4, 5).

7. *Of course any fit to data or to AIM model output can be made much better with additional fitting parameters, and it is not surprising that they are needed to capture solution nonidealities. However, the Abstract must be modified so as not to give the impression that a single parameter is adequate over the entire range of solute composition.*

   As noted above, our additional terms do not employ additional parameters. Furthermore, as shown by Fig. 1-6, our single parameter ν_i is adequate and stays constant over the entire range of solute composition. So, there is actually no need to modify the abstract in this respect.

8. *A third point regards the handling of mixtures of solutes. Most thermodynamic models assume the applicability of the ZSR relation, which states that water contents of binary solutions can be added to estimate the water content of the mixture. Certainly the single-salt parameterizations proposed here could be computed individually and then the water contents added in the same way. The unique advantage of the PK2007 parameterization arises because the same functional dependence on a_w is used for all solutes, and then it can be shown that the ZSR assumption is equivalent to volume weighting the kappas of the mixture components one performing ONE calculation for the mixed-solute water content. This is not possible with the proposed parameterization because the functional dependence on a_w changes with each solute.*

   Indeed this might not only be an advantage of PK2007. We have empirically seen that a mean ν_i compares well with the ZSR approach. However, here we chose to use the ZSR relation because it is well accepted in the community. Mixtures of solutes are subject of the companion paper, which has been published just recently for discussion at GMDD: http://www.geosci-model-dev-discuss.net/4/2791/2011/gmdd-4-2791-2011.html.

9. *Again, as with any parameterization, there is a tradeoff between accuracy and*

computational efficiency. The PK2007 parameterization is very simple and so far appears to work well for water contents at high water activities, such as those accessed during droplet nucleation. However, it is poor in the subsaturated regime for sodium salts, and certainly should not be applied under those conditions without corrections.

We agree that there is a tradeoff between accuracy and computational efficiency. To accommodate the optimal tradeoff we present four types of parameterizations, i.e. equations (17a-d), with two equations (17c-d) as simple and computational efficient as the PK2007 parameterization.

10. *The parameterizations proposed here can likely be shown to be superior for some solutes and over some ranges of water activity. The comparisons to other formulas, however, should be made "apples to apples", that is, single-parameter fits can be compared to each other, and multi-parameter fits need to be clearly identified and their improvements quantified. As pointed out by other reviewers, if computational efficiency over other methods is to be stressed, then appropriate metrics should be presented.*

    Actually we do compare our parameterizations with another single parameter method, i.e. the κ method, in Fig. 3-6. At the same time we compare it with the thermodynamic reference model E-AIM, since our parameterizations are developed for (and applied in) EQSAM4; described in the companion paper. Note that we propose single-parameter water activity parameterizations that can be used to obtain the single solute molalities of various compounds relevant for atmospheric gas-aerosol partitioning modeling. Because the parameterizations are developed for use in thermodynamic models, they have to be compared with more complex, i.e. multi-parameter fits such as the AIM models. The largest potential in terms of computational efficiency can be expected from the single-parameter water activity parameterizations, if applied to calculate the water activity of mixed solutions. ν_i is succesffully applied in EQSAM4 (see the companion paper http://

    www.geosci-model-dev-discuss.net/4/2791/2011/gmdd-4-2791-2011.html), thus far the only single parameter based thermodynamic model.

11. *The parameterization presented here is designed to be implemented in EQSAM4, and so I appreciate that the authors wish to have it documented in the literature and its behavior with respect to a standard (here, AIM) demonstrated. The formulas presented here certainly have merit in representing aerosol water contents and merit publication, although again I recommend that the presentation be revised so that a larger audience can understand how they fit in to the larger picture of how aerosol water contents have been computed in models.*

    Thank you for the suggestion. We will make this more clear in the revision.

12. *In my review I have focused only on one part of the presented parameterization, the bulk solution water contents, which are key to the accurate representation of the equilibrium expressed in equation 1. However, the authors' point is a good one, in that inaccuracies in the computation of (bulk) water content feed back into the calculation of the wet diameter, and thus can result in errors in the magnitude of the Kelvin term. It is of interest to quantify those feedbacks; I would suggest to separate the bulk solution fits from those considering particle size and to demonstrate the individual contributions to error.*

    We intended to show this based on Fig. 3 and 4 (compare with Fig. 1 and 2). In Fig. 1 and 2, the 4 versions of Eq. 17 are compared at Dp $= 1\ \mu m$. In Fig. 3,4 Eq. (17b) is compared to the κ method and E-AIM for different particle sizes. In the revision we will explain this more clearly.

13. *Further, the authors present additional equations for dealing with the variations in dry particle diameter, which are presumably important in their model application. These seem complicated to introduce into a model that deals with an entire distribution of particle sizes, and perhaps more guidance can be given on how this is done in the model (e.g., using a fixed number of bins?) and what uncertainties*

are introduced compared with, e.g., accurate water contents for a full lognormal distribution.

We agree that an application to an entire distribution of particle sizes requires more guidance. We refer to the EQSAM4 companion paper and to the description of our aerosol dynamical model, GMXe (Pringle et al., 2010; http://www.geosci-model-dev.net/3/413/2010/gmd-3-413-2010.html. Note that GMXe treats the size-distribution and calls EQSAM4 for each particle size, i.e. aerosol mode. For a given aerosol mode (size) EQSAM4 calculates the aerosol water content from the ν_i based Eq. (17); which specific equation is chosen depends on the model application.

14. *The Abstract should be revised in accordance with these comments and with the revisions that are made to the manuscript.*

    We will revise it accordingly.

Minor points:

1. *p. 24815, line 16: this statement is incorrect. There are species (e.g., organic molecules) capable of forming aqueous solutions that are not ionic. For example, sucrose has a rather high kappa value.*

   We will delete "ionic".

2. *bottom of page 24816-top of page 24817: The f(RH) method can actually be used to include effects of deliquescence. Since the observed behavior is merely fit to convenient equations, there is not really any theoretical limitation to how complex the fits are made. Further, some effects that occur in "real" aerosols may be implicitly captured in the observations.*

   We agree that the f(RH) method can implicitly account for phase partitioning, if the fits are made from data that include these information. However, the f(RH) method can not explicitly account for phase partitioning. We will change line 1 of p 24817 to "both methods do not explicitly account for gas-liquid-solid partitioning and deliquescence that".

3. *bottom of page 24818, lines 13 on: I would argue that the identification of terms as "Raoult" and "surface" terms confuses the issue since they arise from the simplified (classic) Kohler equation which does not apply over the full range of water contents. I would recommend, as noted above, to separate out the water activity term and the Kelvin term and discuss their contributions to water content separately.*

   We will delete the identification of terms as "Raoult" and "surface". However, the water activity term and the Kelvin term are already discussed separately with Sec. 3.1, 3.2, 3.3.

4. *Please also note the supplement to this comment: http://www.atmos-chem-phys-discuss.net/11/C11479/2011/acpd-11-C11479-2011-supplement.pdf*

   Thank you for the additional figures.

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