Response to reviews

We thank the two anonymous reviewers for their comments.

In the following, the original comments are in presented *italic font* and our responses are in regular roman font. Revisions are given in **bold font.**

Response to referee #1

General comments

Referee: This paper extends the well-known kappa-Köhler framework for surfactant solutions while accounting for bulk-surface partitioning. The paper also gives an explanation for the differences between theoretical predictions and observations. Although the discussion about the differences and the explanation are based on previous studies and do not provide new evidence about the topic, the kappa framework can be very useful for modeling community. In general, the topic is scientifically relevant and within the scope of ACP. The language is also fluent and the text is well organized and written. Therefore, this paper should be published in the ACP after few corrections and clarifications.

Response: We thank the referee for the thoughtful review. We especially thank the referee for taking the time and effort to comb through the equations and notation to help eliminate the (embarrassingly) numerous little mistakes that crept into the discussion article. Some of these mistakes were due to transcription errors from the computer code to the text. To ensure consistency, we re-implemented the code from scratch based on the equations in the text and carefully rechecked all equations.

Specific comments

Referee: Page 22692, lines 9-11: Can this new approach show something that the previous approaches could not show? In general, this work offers a convenient measure (kappa) for surfactant hygroscopicity, but does not provide new information about the role of surfactants or validity of the partitioning model. New experiments would have been needed for that.

Revision: We removed the sentence.

Referee: Page 22701, lines 13-17: For this purpose Γ_{max} *(or* $f\Gamma_{max}$*) can be interpreted as a fitting parameter, so it does not matter if it accurately describes saturation surface excess. The only requirement for the parameters* $f\Gamma_{max}$ *and is that the fitted equation describes concentration dependent surface tension accurately.*

Page 22701, lines 17-27: Using different values for f *should not change the resulting apparent hygroscopicity (see the previous comment), so check the calculations. It should be noted that the analytical solutions for the partitioning equilibrium change when* f *is not equal to one* (Γ_{max})

changes to $(f\Gamma_{max})$ *and* f *is not the dissociation factor* (ν). *This part of the text should be reformulated or deleted.*

Response: We thank the referee for pointing this out. This point is quite clear after following the derivation of Eq. (11) in Raatikainen and Laaksonen (2011) more carefully. Treating f and Γ_{max} as independent, as was assumed in our discussion, is incorrect. We therefore removed this section from the manuscript.

Revision: Deleted discussion regarding this point.

Page 22702, lines 1-3: What about water? Depending on the definition of the surface and the model simplifications, water molecules can have non-zero surface excess.

Revision: We added water to the list.

Page 22702, lines 11-27: This discussion ignores two relevant topics: dynamic surface tensions and implications for microscopic droplets. Dynamic surface tension gives an indication of time scales in bulk solutions. Typically surface tension changes gradually which indicates gradually developing surface phase rather than instant formation after a nucleation step. Even if some bulk solutions (not SDS) need a long time to reach the equilibrium, this can be much faster process for microscopic droplets and especially for the thin surface layer. Especially the dynamic surface tension behavior needs to be discussed here (e.g. connection with the nucleation, observed time scales for reaching equilibrium surface tension and implications for current conclusions).

Response: We significantly revised the paragraph to include explicit discussion on the kinetics of surface tension.

Revision: "An interesting, and perhaps provocative question is whether bulk-to-surface partitioning occurs at the time scale of CCN experiments. Observations show that surface tension gradually decreases with time until equilibrium is reached. The time scale for SDS depends on its concentration, but equilibration time scales are generally < 0.3 s (Kloubek, 1972). This slow equilibration time appears to be consistent with a model that includes kinetics of diffusion to the surface together with the adsorption/desorption on the surface (Chang and Franses, 1995). The time scale can be longer for certain surfactants and is not well understood when stable micelles limit the monomer flux (Patist et al., 2001). During typical CCN experiments an initially dry particle is exposed to maximum supersaturation at time scales ranging from ~1-5 s (Snider et al., 2010). If there are no kinetic limitations to hygroscopic growth and micelle disintegration, and kinetics are not affected by particle curvature, pure SDS particles should have sufficient time to express their equilibrium surface tension in CCN experiments. Kinetic limitations to hygroscopic growth, however, are observed for organic compounds (Sjogren et al., 2007). Further, water contents in SDS droplets at subsaturated relative humidity are well below the critical micelle concentration. Kinetic limitations of micelle dissolution, combined with kinetic limitations of water uptake may lead to non-equilibrium surface tension at the time of CCN activation in laboratory experiments. One indication that kinetic limitation may exist is the absence of evidence of

the non-linear mixing in the presence of counter ions. For example, Prisle et al. (2010) present data for three sodium fatty acid salts mixed with NaCl. The predicted increase in the critical supersaturation at high surfactant volume fraction is not evident in their data, hinting that the surface phase might not have fully formed. The implication is that in the laboratory, surfactants do not alter the surface tension and simply behave like other organic molecules that are not surface active. Whether this is indeed the case, and whether this conclusion would also be valid at the much longer time scales available in actual clouds, will require further detailed investigation."

Page 22703, lines 11-13: Why would Γ_{max} *and* κ_{chem} *not be easily constrained by reliable experimental data? For this purpose,* Γ_{max} *should be considered as a fitting parameter.*

Revision: We removed this statement.

Technical corrections

Page 22689, Equation 1: Units are not matching. Maybe T *should be* T^3 *and the unit of A is K* m^3 J^{-1} *See also the unit of A in Table 1.*

Response: In equation (1) T should be T^3. Indeed the unit of A is $K\ m^3\ J^{-1}$.

Revision: We corrected the mistake.

Page 22690, line 11: Add reference and explain (briefly) AIM

Response: We added a reference and added an explanation.

Revision: "To distinguish these values from the CCN derived techniques, these κ's have been referred to as κ_{Raoult}, $\kappa_{\mathrm{intrinsic}}$, κ_{chem}, κ_{AIM}, or κ_{GF} where the subscript denotes the origin of the data or model used in conjunction with Eq. 2 (Raoult = Raoult's law, AIM = Aerosol Inorganic Model, chem= chemical composition, GF = hygroscopic diameter growth factor data). For example, AIM (Clegg et al., 1998) models a_{w} as a function of the mole fraction of water for some electrolyte solutions, from which κ can be inferred."

Page 22693, Equation 4: Check the equation and possibly remove either volume fraction or subscript i from $V_{s,i}^{b}$

Revision: removed i from $V_{s,i}^{b}$

Page 22693, Equation 5 (upper): Check the equation and possibly remove surfactant volume fraction from the denominator

Response: We rechecked the equation and revised according to the referee's suggestion. Our initial code on which the figures were based did not include this term.

Revision: mistake corrected

Page 22694, line 4: Molarity is moles per volume of solution

Revision: mistake corrected

Page 22695, line 5: Add space to "1generally"

Revision: added space

Page 22696, lines 11-12: Add at least one comma or reformulate this sentence

Revision: added comma (which got lost during typesetting)

Page 22697, line 1: Add right parenthesis after "Eq. (5)"

Revision: added parenthesis (which got lost during typesetting)

Page 22697, line 5: Equation 7 instead of 5

Revision: corrected

Page 22697, Equation 8: Parameter a_0 *depends on* k_2 *and not* ν

Revision: corrected equation in the text

Page 22697, line 17: Change "(n)=0" to "(n=0)"

Revision: corrected

Page 22700, line 22: "must be obtained"

Revision: that section has been removed from the text.

Page 22701, line 2: “surfactants. In”

Revision: corrected (which got lost during typesetting)

Page 22703, line 25: Change CCC to CCN

Revision: corrected

Page 22709-22710, Tables 1 and 2: Moles could be abbreviated as mol

Revision: corrected

Response to referee #2

This paper deals with the complex topic of bulk/surface partitioning affecting the cloud activation potential of aerosol particles. The paper is concise whilst seemingly presenting a reformulation of existing tools to understand the role this phenomenon may have. More work is needed in this area, specifically in going away from proxy systems to understand the behavior of atmospherically complex mixtures. Given the wide uptake of the single parameter representation within aerosol-cloud interaction models, the paper is relevant to the wider audience. Before publication however, some general comments need addressing with respect to its uniqueness. Modelling bulk/surface partitioning is a complex problem. There have been numerous studies in which both iterative and analytical numerical methods have been presented to enable the wider community to probe the sensitivity to this process. From a forward modelling perspective the reader needs some guidance on the clear benefit of this paper when compared to those methods that account for perturbed Raoult and Kelvin contributions to the traditional 'Kohler' curve. The latter methods, which are referenced in this paper, are available for uptake for generalised studies for systems of varying complexity. For investigators that already rely on the single parameter representation, the beauty of that framework is the ability to attempt mitigation of chemical complexity when describing CCN activation potential. If the framework presented here were to be used by others who rely on empirical representations of 'Kappa', there seems to be an inconsistency. There is no reason why that empirical representation wouldn't already account for partitioning if it was derived from a CCN based measurement. Is this true?

Response: The referee is correct that κ_{app} as defined via Equation (1) implicitly accounts for partitioning effects. It is not accounted for in κ values that are determined from water activity measurements alone, i.e. if values are derived via Equation (2), as is outlined in the discussion of that equation.

Revision: We revised the introduction (pg. 22689) to make the point more clearly that equation (1) can indirectly account for partitioning effects.

"The approximate relationship between the dry particle diameter (D_d), the critical saturation ratio (S_c), and κ is given by (Petters and Kreidenweis, 2007).

$$\kappa = \frac{4A^3\sigma_{s/a}^3(T)}{27T^3D_d^3\ln^2 S_c}, \qquad \mathbf{(1)}$$

where A= 8.69251 10^{-6} K m^3 J^{-1}, $\sigma_{s/a}(T)$ is the temperature-dependent surface tension of the solution/air interface, and T is temperature. The so-found κ has been referred to as κ_{CCN}, $\kappa_{effective}$, or $\kappa_{apparent}$ (κ_{app}) to specify that the value has been derived from CCN measurements and/or that a constant temperature-dependent surface tension was assumed in the calculation of κ from an S_c, D_d pair (Pöschl et al., 2009, Sullivan et al., 2009a, Christensen and Petters, 2012). The semi-empirical characterization of CCN activity in terms of κ_{app} if a self-consistent set of surface tension and temperature is applied when computing S_c values from experimentally determined κ_{app}. This holds true even if the assumed value for $\sigma_{s/a}(T)$ is incorrect. In this case κ_{app} is simply a parameterization that implicitly accounts for surface tension effects. Equation (1) is valid for κ > 0.2 (Petters and Kreidenweis, 2007), but may be used for κ > ~0.01 if small numerical errors are acceptable. One utility of κ_{app} is that changes in κ_{app} can be related to changes in chemical composition

via chemical reactions (Petters et al., 2006; George and Abbatt, 2009; Jimenez et al., 2009; Sullivan et al., 2009b) or mixing with other compounds (e.g. Gunthe et al., 2009; Dusek et al., 2010) and thus it can be used as vehicle to parameterize the effect of these processes on CCN activation in models (Lohmann and Hoose, 2009).”

On the other hand, if a theoretical representation of ‘Kappa’ were used, then steps to calculate each ‘kappa’ value are techniques that one would use in traditional Kohler theory. Reading the end summary, which is very nicely caveated, it should be obvious to the reader if the sole aim of this work is to allow large-scale modellers who currently incorporate Kappa Kohler theory to test the sensitivity to bulk to surface partitioning.

Response: We slightly disagree with the referee on this point. We agree that this extension may be useful for the modeling community, including the type of sensitivity tests outlined by the referee. However, one of our main aims was to clarify how kappa values derived from chemical measurements (e.g. water activity or hygroscopic growth factors) can be used to compute critical supersaturations.

Revision: None

Regarding this, the recent study by Prisle et al (2012) shows the potential effect of choosing a detailed bulk/surface partitioning framework over a simplified framework in a global climate model. This is the kind of work that needs performing, on multiple scales, to decipher what level of complexity is required. That study, which should be referenced, showed that existing parameterisations can be used in large-scale models to test the importance of complexity and dictate avenues for future investigations. It further supports the comments made by the authors in this paper that more investigations are needed. As a process level diagnostic tool, the other methods presented in the literature must also be used to look at, for example, non-ideality in both phases, choice of dividing surface etc

Prisle, N. L., et al. (2012), Surfactant effects in global simulations of cloud droplet activation, Geophys. Res. Lett., 39, L05802, doi:10.1029/2011GL050467.

Response: We fully agree with the referee on this point and added additional discussion.

Revision: “The equations presented here can used to perform simulations to determine the degree of complexity that must be included in (global) model simulations. For example, Prisle et al. (2012) demonstrate that the sensitivity of simulated cloud droplet number concentration to the presence of surfactants is small in the ECHAM5.5–HAM2 model if surfactant partitioning is included. Aside from model applications, our equations can be used as a starting point for process-level diagnostic studies. For example, it is straightforward to evaluate the extent to which discrepancies between κ_{chem} and κ_{app} can be attributed to surfactant properties. Absence of closure within this simplified framework should trigger in-depth scrutiny of the underlying assumptions, e.g. non-ideal behavior in all phases, the choice of the dividing surface, kinetic limitation, or the assumption of zero surface excess for the non-surface active species.”

Minor comments:

Section 3.3, page 22700, line 18: Presume this should be ‘practice’.

Revision: Corrected

Page 22701. Line2: Missing a ‘.’ after surfactants.

Revision: Corrected (this was lost in typesetting)

Page 22688, line 19: Kohler theory assumes all of the solute material is involatile also.

Revision: We added this to the sentence.

Line 20, ‘Text book versions’. Please add a reference.

Revision: We added a reference to the sentence.

Abstract: Remove the unreferenced reference to ‘Raatikainen and Laaksonen’. Suggest either fully referencing or alluding to past work in a more general sense.

Revision: We removed the reference from the abstract.

Page 22689, line 5: Please re-iterate the conditions (k) for which this approximation is valid.

Response: We added this caveat.

Revision: Please see our revised paragraph to the first general comment.

Section 2.3, page 22696, line 12: Add comma after ‘surfactant’.

Response: We edited this section.

References added

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