Author's response to Editor's report for the revised manuscript "A predictive thermodynamic framework of cloud droplet activation for chemically unresolved aerosol mixtures, including surface tension, non-ideality, and bulk/surface partitioning"

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I thank the editor for her time and additional comments and suggestions for improving the manuscript. Comments to each point and corresponding changes made in the revised manuscript are given below, indicated in blue. Comments to specific suggested changes provided in separate .pdf file of manuscript version6 are provided directly in this document.

General comments

I appreciate your revisions and responses to the referees' and my previous comments. I still have numerous comments. As a major issue remains the lack of focus and the demonstration of the extent to which the presented framework improves CCN predictions as compared to previous models. As the manuscript reports on 'new developments or novel aspects of experimental and theoretical methods and techniques that are relevant for scientific investigations', it will qualify after revision for a Technical Note. However, unless it is significantly revised and rewritten, I cannot see 'substantial advances and general implications for the scientific understanding of atmospheric chemistry and physics'as it would be required for a Research Article. Please note that the manuscript title should start with 'Technical Note:'.

The manuscript has been significantly revised and rewritten, to clarify each of the remaining points detailed in the Editor's report and the annotated version6 of the manuscript. Major revisions have been made of Abstract, Introduction, Section 2.3 / version6 (now Section 2.4) concerning the relation between the presented full partitioning model and the simplified models, Section 3.4 / version6 (now Section 4: Discussion), and the Conclusions. Due to the large number of changes, I refer to the track-changes file for specific details. As it was indicated in communication from the Editor that a final decision regarding

Research Article vs. Technical Note is pending review of these revisions, the manuscript title has not yet been modified accordingly.

1. It would have helped a lot in the author's response if you clearly stated in which lines and sections you changed text and how you addressed the referee comments.

   The amount of revisions were so substantial and many comments were addressed in multiple places throughout the revised manuscript. Because of this, it was not possible to list each explicitly and in a concise manner within a reasonable amount of time. The sections were listed and specific changes could be followed most easily in the track-changes document. Further revisions in response to specific comments are now clearly indicated in the following.

2. Many sentences are very long. While this is, of course, a personal choice and writing style, it makes reading often very difficult. It might also add to the lack of conciseness that was criticized in the previous referee reports.

   Long sentences are an unfortunate personal writing style. I have tried to shorten and divide sentences throughout the revised manuscript. However, this has unfortunately added more word to convey the same ideas.

   I do not think that the comment by Referee #3 has been sufficiently addressed "Overall, the manuscript is too long, difficult to follow, and the discussion regarding the implication of the model is overreaching....If the manuscript were shortened, and focused more on under what conditions and applications the different levels of partitioning treatment are needed, it would be a useful contribution to the field."

   The reviewer's comment suggests a discrepancy between the intended aim and focus of the manuscript and what is perceived. The original aim was to introduce the model and illustrate its application and how it could be used to gain detailed insight into the various effects of surface activity on hygroscopic growth and activation, directly for chemically complex and unresolved aerosol mixtures - including also actual atmospheric samples.

   While "conditions and applications the different levels of partitioning treatment" has been the focus of our previous work using thermodynamically consistent, predictive modeling for well-known compounds (such as the fatty acid salts), it was not intended as the main focus of the present work. The present work introduces a framework that enables thermodynamically consistent, predictive modeling for complex (higher order) mixtures comprising compounds that are not well-known (unresolved). The aim is to demonstrate its use and to validate it against CCN measurements. The model can be directly applied to any mixture, including atmospheric aerosol samples. NAFA was chosen as an example of a surface active mixture of compounds without well-known chemical identity and compound-specific properties. It has atmospheric relevance as previously establish model mixture for atmospheric HULIS, which is a major class of atmospheric surface active organic aerosol. NAFA was furthermore used, because all the necessary data for enabling the calculations was available in the literature. These motivations are described in the Abstract (p.1 18–20) and Introduction (p.6 l.9–25). By obtaining similar data for other atmospherically relevant, complex mixtures, thermodynamically consistent, predictive modeling can be made directly for these mixtures as well. This will allow us to assess the impact of each of the effects of surface activity (partitioning, surface tension reduction, bulk phase depletion) separately, directly for the samples in question, without retro-fitting model parameters or assuming thermodynamic properties from a proxy.

In response to the reviewer's request, Sections 3.4.1, 3.4.2 and 3.4.5 / version6 were introduced to discuss various aspects of ”under what conditions and applications the different levels of partitioning treatment are needed”. This discussion has now been significantly revised and clarified in Section 4: Discussion, under Sections 4.1 ”Effects of surface activity for the predicted CCN activity of NAFA” and 4.1.1 ”Validity of assumptions in simplified predictive frameworks for NAFA” (specific results of the present work), 4.1.2 ”Conditions favoring reduced droplet surface tension” (includes discussion of which more general conclusions can be made), and 4.3 ”Potential for large-scale applications” (what can be inferred regarding large-scale applications).

Calculations with an additional simplified model (the ”Insoluble surfactant” model, Section 2.4 and S1) and detailed calculations of Köhler curves and droplet properties along the Köhler curves (Sections 3.3 and S3) were also added in response to the reviewer's request, significantly increasing the lenght of the manuscript and the detail of the discussion.

The manuscript length has not changed

It has been challenging both in the present and several previous revisions to shorten the manuscript while adding further clarifications, discussion points, references, and at the same time also retaining the original results and information requested during previous stages of review. Therefore, even if previous text has been shorten, focused, moved to the SI, or deleted, the length of the manuscript has continued to increase. New section headers have been added to assist in addressing requested clarifications and elaborations, which have also added to the overall length of the manuscript.

Specifically for the present revision, Section 3.4.4 and parts of Section 2.2.1 / version6 were moved to the supporting information (SI), but not removed entirely from the manuscript as they contained information requested and referenced in previous responses to reviewers. Subsection header was added for the text describing the Köhler model (Eq. 1), to help clarify the relation between the general (mass-based) Köhler model, the full mass-based Gibbs partitioning model (Eq. 6), and the simplified frameworks described in Section 2.3 / version6 (now Section 2.4). Section 3.4.2 / version6 was changed to Section 4.2 and subsection headers were added for each of the partitioning frameworks discussed.

and instead of a concise and clear discussion of the model's novelty and need, I am still left with questions such as
-for which compounds does it need to be applied? You state in the introduction that previous models perform well for common aerosol surfactants.

I sincerely hope that the discussion and other relevant sections have now been sufficiently clarified to address the remaining questions.

The presented model is intended for predictive, thermodynamically consistent Köhler model calculations, for aerosol mixtures where the chemical composition is not well-defined. Previous predictive, thermodynamically consistent Köhler models have performed well for a few well-known surfactants in simple, well-defined mixtures. For complex mixtures, the models cannot be applied in the same form. Instead, other models have then used A) simplifying assumptions (predictive, but not thermodynamically consistent, Section 2.3 / version6), B) retro-fitting of model parameters (thermodynamically consistent, not predictive), or C) assuming a sufficiently simple proxy system (predictive and thermodynamically consistent, but not made directly for the actual system in question).

This has been clarified in the Abstract, Introduction, Conclusion, and Sections 2.4, 4.1.1, and 4.2 of the revised manuscript.

-under what conditions does it outperform previous simpler approaches? Throughout the manuscript (e.g. Figures 1and 2) you show that previous simpler models give nearly the same results. Why do we need the full partitioning model?

The full partitioning model is needed to make thermodynamically consistent, predictive calculations for aerosol mixtures where the chemical composition is not well-defined. Thermodynamically consistent, predictive calculations are needed to specifically resolve the different effect of surface activity. The simplified frameworks are based on *a priori* assumptions regarding at least one of these effects. The analytical models may confound impacts of several effects (e.g. water activity and surface tension) in the obtained model parameters.

The simplified models work well, when the underlying assumptions are valid. The full partitioning model outperforms the simplified models when they are extended beyond the range of validity of the underlying assumptions. The full partitioning model is needed to independently confirm the conditions when the assumptions of the simplified frameworks are valid. In other conditions, good performance of the simplified frameworks and analytical model parameters could be coincidental. When analytical model parameters are extended to other conditions (different aerosol mixtures, humidities, particle sizes), these fitting parameters are no longer strictly valid. The range of conditions where they remain a suitable approximation can only be confirmed by new experiments or independent, thermodynamically consistent predictive modeling.

Without the full model calculations, there is no confirmation that the simplifying assumptions are actually valid for the aerosol mixtures and conditions in question or whether good model performance is accidental.

The performances of the simplified models with respect to the full model, as well as CCN data, are discussed throughout Section 3 and summarized in Section 4.1.1 and the Conclusions (p.32 l.16–29) of the revised manuscript.

-for what mixtures is it relevant?

The model is relevant for all surface active mixtures, and was in particular intended for surface active mixtures of unknown composition, such as atmospheric aerosol samples, because thermodynamic previous frameworks do not enable predictive calculations for such mixtures.

–e.g. in Figure 1, it looks like that ≥80% NAFA particles are well represented by model (K) and (S). How likely is it that atmospheric particles are composed of >80% surface active compounds?

The models (K) and (S) give good agreement with experimental data for aerosol mixtures with ≥80% NAFA. Comparison to the full model show that for the NAFA mixture, these are the conditions where the underlying approximations of the simple models are reasonable. There is no reason to assume that all surface active compounds and mixtures found in atmospheric aerosols will behave similarly to NAFA. On reason is of course that other mixtures will likely have different surface activity. They also exhibit different non-ideal interactions in response to changing droplet state. Because of this, the conditions where the assumptions of the simplified models apply will most likely be different for other mixtures than for NAFA. The question is complex, and thermodynamically consistent, predictive modeling, such as with the presented framework, is needed to explore and resolve the various aspects of surface activity for different aerosol systems.

I hope the intended use of the presented model, and the relation of the presented results for the NAFA system is clear from the careful revisions of the manuscript, e.g. in Abstract (p.1 l. 1–3, l. 18–20, p.2 l. 7–9), Introduction (p.6 l.9–25), Discussion Section 4.1.2, and Conclusions (p.31 l.30–p.32 l.15).

3. In your author's response, please state why the second author has been removed from the manuscript so that this change is documented in the openly accessible files.

   Bjarke Mølgaard made the parametrizations for surface tension and water activity described in Section 2.2 /version6 under my supervision. He since left academia, now more than 5 years ago, and has not contributed further to the work. He has not taken part in the model implementation, modeling, analysis of results, or preparation of the first and revised manuscript versions and author responses. While he approved the initial submission, he has not wished to be further involved in the work or or to remain as an author on the work. His contributions have been acknowledged in the Acknowledgement section of the revised manuscript, according to his own wish. A statement to this effect has also been provided to the Editor and editorial office on 25.1.2021.

Specific comments

1. p. 1, l. 9: 'allow for a description of chemically unresolved mixtures '–something seems to be missing here: 'the description of water uptake or surface partitioning or...?'

   The text has been modified to "Contrary to previous thermodynamic frameworks, it is formulated on a mass-basis to obtain a quantitative description of composition-dependent properties for chemically unresolved mixtures."

2. p. 1, l.4: What 'different mechanisms'are referred to here?

   The text has been modified to "...the impacts of different effects driven by surface activity, in particular bulk/surface partitioning and resulting bulk depletion and/or surface tension reduction, on aerosol hygroscopic growth and cloud droplet activation remain to be generally established."

3. l. 17-19: Is this a finding from the current study or common knowledge?

   This is a result from the present work using the presented model. The text in the Abstract has been modified to clarify this: "The presented framework predicts a similar influence of surface activity of the chemically complex NAFA on CCN activation as was previously shown for single, strong surfactants. Comparison to experimental CCN data show that NAFA bulk/surface partitioning is well represented by Gibbs adsorption thermodynamics. Contrary to several recent studies, no evidence of significantly reduced droplet surface tension at the point of activation was found. Calculations with the presented thermodynamic model show that throughout droplet growth and activation, the finite amounts of NAFA in microscopic and submicron droplets are strongly depleted from the bulk, due to bulk/surface partitioning, because surface areas for a given bulk volume are very large. As a result, both the effective hygroscopicity and ability of NAFA to reduce droplet surface tension is significantly lower in finite-sized activating droplets than in macroscopic aqueous solutions of the same overall composition."

4. l. 20-22: Does this mean that previous models that account for Gibbs adsorption are equally good or is the current framework the first that uses this adsorption?

   Several previous frameworks have used Gibbs adsorption thermodynamics. However, they require that the identity and specific amount of all chemical species in the mixture are known and typically assume ideal or pseudo-ideal mixing interactions between different components. To my knowledge, the presented framework is the first to apply Gibbs adsorption on a mass-basis to perform calculations directly for a chemically complex and unresolved mixture, and it accounts for effects of non-ideal interactions on water activity in the Köhler equation. The Abstract has been modified as indicated in the point above to help clarify this. It is also reflected in the title.

   Reference to previous Gibbs adsorption based models is explicitly made in Section 4.2.3 "Gibbs adsorption models" p.29 l.20–22 of the revised manuscript:
   "Partitioning models based on Gibbs adsorption with Szyszkowski-type surface tension equations have been the most widely used in predictive Köhler models (see e.g. Malila and Prisle, 2018), however, the present framework is the first to implement this approach on a mass-basis."
   Furthermore, p. 3 l.32–33 mentions:
   "An overview of the most widely used partitioning models in connection with Köhler theory is given by Malila and Prisle (2018). "

5. p. 3, l. 16-18: This sentence is not clear. 'Köhler calculations'is not a common expression. Do you mean that 'hygroscopic growth of particles'?

   'Köhler calculations' has been clarified until introduction of the specific model equations in Section 2 as "calculations of the cloud forming potential of surface active aerosol using Köhler theory" (p.3 l.30–31) or "model calculations using Köhler theory".

   Is the sentence saying that commonly equations for surface/bulk partitioning are used that were derived based on bulk solutions rather than droplets?

No. The partitioning model and the Gibbs adsorption equation (Eq. 6) is the same for all solutions, macroscopic and droplets.

The sentence explains why the partitioning model is needed and how it is used. It has been modified (p.3 l.30–32 of the revised manuscript) to clarify this: ”Due to size-dependent effects of bulk/surface partitioning, in calculations of the cloud forming potential of surface active aerosol using Köhler theory, macroscopic solution property–composition relations must be connected to those of growing microscopic droplets with changing A/V *via* a partitioning model.” Furthermore, in Section 2.3 on p.9 l.20–21 of the revised manuscript is explained: ”The partitioning model is the key to applying composition-dependent properties obtained for macroscopic systems to finite-sized droplets.” This aspect has also been elaborated in the first response to reviewer 2.

6. p. 3, l.33–p.l. 15: This part of the introduction is very exemplary for the confusion and unclear message regarding the novelty of the study throughout the whole paper:

   -l. 33, you state that the CCN predictions for common aerosol surfactants work well but might be too simple as they only consider binary or ternary mixtures.

   The previously presented thermodynamically consistent frameworks have worked well for a few selected, well-known single compounds or simple, chemically well-defined mixtures. These systems, however, are likely not fully representative of atmospheric aerosols, which are expected to be chemically more complex. None of the previous models have been shown to work well for a range of different surface active compound classes found in the atmosphere. The thermodynamically consistent frameworks also have not be applied to unresolved aerosol mixtures. They require the chemical identity and amounts of all compounds in the mixture to be known, or assumed. When the mixtures contain a larger number of different chemical species, the model may become too complex to solve, even if the identities, quantities, and properties of all compounds are known. This knowledge is in practice also not available.

   This is exactly what motivated the present work.

   -p. 4, l. 2: you state that mixtures in atmospheric aerosol are likely much more complex.

   Yes, atmospheric aerosols likely contain more than 1 surface active compound and 2–3 different compounds altogether.

-p. 4, l. 13: Here, you refer again to one proxy compound.

Simple mixtures were here referred to as one common approach to tackling the chemical complexity of aerosols found in atmosphere and more elaborate laboratory experiments, by using simple, well-known compounds or mixtures (proxies) to approximate the thermodynamic properties of the complex, unknown mixture. Likely, this is insufficient as a general approach to modeling complex aerosols, for the same reasons described above.

It may also not be valid to use single compounds as proxies for mixtures, simply because the response to changing conditions is singular, rather than gradual. This is well-known in thermodynamics and has been noted in previous work (Prisle et al., 2012a) which is referenced on p.29 l.9–10 of the revised manuscript: "As discussed by Prisle et al. (2012a), if the proxy mixture is too simplistic, predicted properties may be more sensitive to variations in the droplet state, compared to the actual complex mixture."

As this part of the introduction should set up the motivation of your study, it should clearly state why (i) fatty acids are not sufficiently good proxies (for which there are obviously good models), (ii) your proxy compound is more representative than fatty acids to represent aerosol surface activity.

This is not exactly the point of this work.

Fatty acids are present in the atmosphere and may be good proxies for atmospheric aerosols that comprise a lot of fatty acids or structurally similar surface active compounds. But they cannot *a priori* be used as proxies for all surface active material in the atmosphere without reasonable confirmation that they represent the behavior of many different surfactants and their atmospherically relevant mixtures in different conditions.

There is no reason to believe without broad explicit confirmation that all surface active atmospheric aerosol components will behave as fatty acids in cloud droplet activation. Our previous work using thermodynamically consistent, predictive modeling for single, well-defined compounds has shown significant differences in the cloud droplet activation of different fatty acids even within the same homologous series, as well as between different compound classes.

The point of this work is not to suggest NAFA as a better proxy for atmospheric aerosols. The NAFA mixture is used as an example to illustrate how the presented framework enables thermodynamically consistent, predictive modeling of aerosols comprising a chemically complex mixture of unknown exact chemical composition. The presented framework can be applied to surface active atmospheric aerosols in an analogous fashion. As described above, the NAFA mixture was selected due to the ready availability of the necessary experimental data (CCN activation, water activity, surface tension) and its relevance as previously used model system for atmospheric HULIS, which is an important class of atmospheric surface active organic aerosol. NAFA is merely one chemically complex, unresolved mixture used to illustrate the application of the presented framework. The presented model may be applied to actual atmospheric mixtures, using an analogous approach as outlined in this work.

This part of the introduction has been thoroughly revised (p.3 l.30–p.5 l.35), to hopefully clarify these aspects. This motivation is followed by an outline of the aim of the present work, introducing the model p.6 l.1–8 and the application to NAFA mixtures p.6 l.9–25.

7. p. 8, l. 15 (Section 2.2.1): It would be much easier to follow if all parameters in Eq-8 were presented together and not one page later. I suggest restructuring this section and only presenting the relevant information.

   The section was restructured as suggested. At the same time, discussions of different surface tension measurement times was moved to Section S5 of the revised SI together with Section 3.4.4 / version6, to shorten the main manuscript. Please see also response to comment about Section 3.4.4 / version6 below.

8. p. 10: Section 2.3: It would help a lot if you clarified here which of the models have been used before and which ones are new in the current study. Just reading this section, I assumed that (P) is the novel part of the current study, and (B) and (K) represent simplifications of it. Brief clarifications like this would immensely help to identify the novel parts of the study and how they are related to each other.

   Section 2.3 / version6 (now Section 2.4 in the revised manuscript) has been renamed to "Comparison to simplified predictive models" and "representation" has been replaced with the simpler "model" in most instances throughout the manuscript, to clarify the relation between the simplified models and the detailed model presented in this work. The following text was added/modified in the beginning of Section 2.3 / version6, in order to clarify the aim and role of calculations with the other model representations in relation to the model presented in this work:

   "The framework presented in Sections 2.1 and 2.2 enables predictive, thermodynamically consistent Köhler calculations of droplet growth and activation for chemically complex and unresolved surface active aerosol mixtures. In this framework, droplet growth and activation In this framework, droplet growth and activation is influenced by several simultaneous processes in the aqueous phase, including dilution, bulk/surface partitioning, reduced droplet surface tension, and non-ideal water activity. To highlight the interplay and relative roles of these different underlying mechanisms, Köhler calculations for NAFA–NaCl particles using the full mass-based partitioning model are compared to several simplified predictive approaches (outlined below and summarized in Table 1). Two frameworks are used, which consider bulk/surface partitioning in a simplified and not thermodynamically consistent way. Of these simplified partitioning frameworks, one (labeled I, as explained below) furthermore considers surface tension reduction in the droplet, however also in a not thermodynamically consistent way, whereas one (labeled S) does not consider reduced droplet surface tension. Additionally two frameworks are used, which do not consider bulk/surface partitioning in the droplets. These bulk solution models are thermodynamically consistent, but the application of thermodynamic relations derived from macroscopic measurements to describing microscopic droplets using these models is not. Of the two bulk models, one (labeled B) considers reduced droplet surface tension, and one (labeled K) does not.

The simplified predictive frameworks are implemented using the same mass-based Köhler model (Eq. 1) as the full partitioning model presented in this work (labeled P). For each NAFA–NaCl dry particle composition and size, cloud droplet activation is therefore calculated from Eq. 1 according to five different representations:"

Table 1 has been updated to further support these clarifications.

Model (P) is indeed the novel part introduced in the current study. The text on p. 10 l. 17 / version6 has been changed to:
"The thermodynamically consistent, full partitioning model, considering reduced droplet surface tension and non-ideal water activity, presented in this work (Sections 2.1, 2.2, and 2.3)."

Model (S) was introduced by Prisle et al. (2011), as indicated.

Model (I) was a novel addition to this work, following the request of reviewer 2 to represent an insoluble surfactant. It uses a similar approach as Davies et al. (2019), as indicated. The model was not successful in reproducing variations in measured CCN activity for the NAFA–NaCl particles and results are presented in Section S1 of the SI.

Models (B) and (K) are not simplifications of (P), they are bulk solution models that do not include bulk-surface partitioning. Similar approaches have been used in our previous work (Prisle et al., 2010) but not in a mass-based application. This has been further clarified with the changes mentioned above at the beginning of this point.

For model (B) has been added the text: "Similar approaches have been used in numerous previous works (e.g. Shulman et al., 1996; Facchini et al., 1999; Harmon et al., 2010; Kristensen et al., 2014), but have been demonstrated to lead to significant overestimations of CCN activity for simple particle mixtures comprising chemically well-defined, strong surfactants (Sorjamaa et al., 2004; Prisle et al., 2008, 2010)."

For model (K) has been added the text: "Similar approaches are commonly used in cloud microphysics, when aerosol surface activity is unknown or considered to have minor influence on CCN activity (see e.g. Prisle et al., 2012a; Kristensen et al., 2014)."

9. p. 15, l. 21: I do not understand how surfactants can enhance hygroscopicity. Hygroscopicity is a bulk property and expressed by the Raoult term, but reduced surface tension affects the Kelvin term. Do you mean 'enhanced water uptake'or do you mean that the amount of soluble mass in the bulk is reduced because of surface/bulk partioning?

   "Hygroscopicity" has been changed to "water uptake" as suggested. Because surface tension and intrinsic hygroscopicity cannot be directly resolved in experiments, reduced surface tension can be considered to enhance effective hygroscopicity, as determined from the observed water uptake. I agree this was not immediately clear.

10. p. 17, l. 28; p. 19, l. 10: 'effects' should be singular. There is only one Raoult effect and Kelvin effect, respectively.

    I meant to say "effects (of NAFA surface activity) on the Raoult term". I agree it was not clear. It has been corrected in the title of Section 3.2.1 "Effects of surface activity on the Raoult term" and throughout the text and similarly for Section 3.2.2 "Effects of surface activity on the Kelvin term" of the revised manuscript.

11. p. 21, l. 4: 'Gibbisan'?

    Thanks for noticing. Corrected to "Gibbs adsorption" for clarity.

12. p. 23, l. 35ff: 'When macroscopic composition-dependent relations for surface tension, as well as other solution properties, are connected to microscopic droplet states via a bulk/surface partitioning model, the effect of bulk/surface partitioning in droplets is to move the solution mixing state to a different point in the composition domain, as illustrated in Figs. 2 and S2 for the present case of NAFA–NaCl droplet mixtures'–please reword this sentence and reduce it to its main message

    The sentences has been changed to "The role of a partitioning model is to *connect* composition-dependent relations for surface tension, as well as other solution properties, derived for macroscopic systems to microscopic droplet states. Specifically, the effect of bulk/surface partitioning in droplets is to move the bulk phase mixing state to a different point in the composition domain, compared to a macroscopic solution with the same total composition. This is illustrated in Figs. 2 and S2 for the present case of NAFA–NaCl droplet mixtures."

13. Section 3.4.2: What is the main message of this section? It seems like a text that should belong to an introduction. How does this text support

or reject any of the previous or presented models? The fact that surface active organics are present in atmospheric particles had been stated before

Section 3.4.2 / version6 was added in response to request by reviewer 2 for discussion of previous works, including some explicitly mentioned, as well as a discussion of the atmospheric implications of the present results and what they indicate about where in the atmosphere partitioning effects might be important. Part of the text (p.24 l.14–p.25 l.1 / version 6) reviews recent results of experimental works for aerosols which are chemically more complex than the simple mixtures with fatty acids and industrial model surfactants, and/or present evidence for reduced surface tension in the droplets, contrary to predictions with the thermodynamically consistent models for simple, strong surfactants. These results have contributed to motivate the present work, because a thermodynamically consistent, predictive framework for unresolved mixtures is needed to resolve the effects of surface tension, bulk/surface partitioning, intrinsic hygroscopicity, and non-ideal water activity for such systems. This text has been merged with the Introduction (p.4 l.25–p.5 l.12 of the revised manuscript).

It is not the aim of this work to support or reject any of the previous models, which all have unique merits and useful applications.

14. Section 3.4.3: How much if this information has been discussed in the previous sections of the paper? How would the current model improve previous predictions?

    Section 3.4.3 / version6 has been carefully revised for repetition of information. It was renamed Section 4.2 ”Comparison to other bulk/surface partitioning models” in the revised manuscript. The comparison of the presented model to other, recently presented frameworks was requested by reviewer 2. Mention of these works in previous sections (now Introduction) focus on the experimental results and the conclusions made from comparison of experimental results with the different models. This section focuses on the differences in structure and assumptions of the models, in relation to the presented framework. Because of these differences, it is not immediately possible to compare the different models for a common test system. For example, the model of Ruehl et al. (2016) is analytical and model parameters cannot be obtained for NAFA from available data. The model of Ovadnevaite et al. (2017) uses a proxy mixture to enable predictive LLPS modeling with AIOMFAC. AIOMFAC parameters are not available for NAFA and no proxy mixture to emulate NAFA aqueous interactions in AIOMFAC have to my knowledge been identified. Because of these challenges, a direct comparison of the presented framework with these models is out of scope of the present work. It is, however, the topic of other new work from our group (Vepsäläinen et al., 2021).

    As mentioned earlier, the presented model is not intended to improve the previous results, but to enable calculations which cannot be made for with the previous models (predictive, thermodynamically consistent, and directly for a complex surface active mixture).

15. Section 3.4.4: If you want to highlight the importance of surface tension effects for cloud droplet formation,not the residence time in the CCN counter is of importance, but the time a particle spends in an updraft below cloud up to cloud base. During this ascent, the relative humidity (saturation) is constantly increasing and the time between a high saturation(¿ 0.9) to cloud activation (i.e. S = 1 or slightly above) is only a few seconds. A few words along those lines would be helpful here.

    Section 3.4.4 / version6 was added in response to comments by reviewer 1. It has been moved to Section S5 of the revised SI and the following sentence was added: ”In the atmosphere, the time a particle spends in an updraft below cloud up to cloud base is also on the order of only a few seconds, similar to the residence time in the CCN counter. It is therefore conceivable, that dynamic effects could have similar impact in the atmosphere as predicted by Lin et al. (2020).”

16. p. 30, l. 14 ff: I do not understand the relevance of surface reactions in the context of cloud processing. These topics seem very hand waving and vague. Cloud droplets have diameters of several micrometers; they are certainly not submicron droplets. The diameter of cloud droplets is thus 100 times larger than that of a dry particle(e.g. 100 nm particle grows to 10 micron droplet), which means that its surface is10,000 larger. It seems unrealistic to me that there is sufficient surface active material in CCN to affect surface tension of cloud droplets. Therefore, extensive surface partitioning does not seem likely as the dilution of the bulk phase is completely different than in non-activated particles. For which curvatures (i.e.droplet diameters) does the Young-Laplace equation apply? Is it relevant for cloud droplet sizes? What is known about pressure-dependence of aqueous phase reactions under atmospherically relevant parameter ranges? Unless you can bolster any of these effects by either reasonable estimates or references, I suggest removing these speculations.

    The relation of surface partitioning to surface (and bulk) reactions in droplets is mentioned in the Conclusions as an outlook from the current work, which should be clear from the text. It addresses ongoing work by my research group and the atmospheric chemistry and aerosol community, therefore it should be of interest to the community to draw this connection to the presented work. As an outlook, it will inherently be more ”hand-waving”. It has been mentioned since the first draft and not explicitly commented in the earlier revisions. For these reasons, I prefer to keep it. A few additional clarifications and references have been added to the text as requested:

    ”Surface activity of aerosol components may also have important implications for other processes related to cloud microphysics, including aqueous chemistry occuring as droplets repeatedly shrink and grow during cloud processing in the atmosphere (Pruppacher and Jaenicke, 1995). For example, owing to the relatively large surface areas of sub-micron droplets, aqueous surface chemistry, such as the photosensitized limonene uptake by Humic Acid, another atmospheric model HULIS mixture (Tsui and McNeill, 2018), may be significantly enhanced, compared to reactions in the bulk phase. Furthermore, extensive surface enrichment due to partitioning will change the chemical environment and possible chemical reaction pathways and rates of surface active species in both the surface (Prisle et al., 2012b; Öhrwall et al., 2015; Werner et al., 2018) and for droplets in the sub-micron range (Prisle et al., 2010) also in the bulk phase. When depleted from the droplet bulk, surface active compounds will not be as readily available for reactions with soluble species in the aqueous droplet phase and the rate determining concentrations will be vastly different from a macroscopic solution with identical total composition. Finally, pressure-sensitive reactions in the droplet phase (Jenner, 1975) will be impacted by the elevated pressures inside microscopic systems from the finite curvature radii according to the Young-Laplace equation (Adamson and Gast, 1997). This pressure elevation, which is also the basis for the Kelvin effect in Eq. 1, depends directly on the droplet surface tension. The present work shows significant differences of up to roughly a factor 2 between predicted surface tensions for sub-micron droplets and macroscopic solutions, translating to a factor of 4 difference in the curvature effect on chemical potential, which must be taken into account together with the explicit curvature variation in efforts to constrain such effects on yields and pathways of aerosol chemistry (e.g. Tu and Johnston, 2017; Winkler et al., 2012)."

Throughout the manuscript, surface activity is discussed as being manifested through both bulk/surface partitioning and surface tension.

Even macroscopic solutions of atmospheric surfactants can have significant surface enrichments at highly dilute concentrations, which may affect chemical reactivity in the surface (Prisle et al., 2012b; Öhrwall et al., 2015; Werner et al., 2018).

Cloud droplets grow and shrink multiple times during cloud processing (Pruppacher and Jaenicke, 1995) and therefore also spend time in sub-micron sized states where both surface and bulk compositions are affected by partitioning.

The Young-Laplace equation (Adamson and Gast, 1997) is the basis for the Kelvin effect and relevant for sub-micron growing/shrinking droplet sizes.

The pressure-sensitivity of aqueous reactions is well-known (Jenner, 1975), but the implications for atmospheric chemistry is currently being explored.

It is therefore relevant to draw the connection to the results of the present work.

Additional changes

In addition to the changes described above, the following changes were made:

1. p.1: My affiliation has changed.
2. p.1: The Abstract and Conclusions were revised to emphasize the novelty, aim and results of the work.
3. p.5: A subsection header was added for "2.1 Köhler theory" to highlight the common part of the different frameworks used.
4. p. 10 l.20–23: The text "By using measurement-based parametrizations, which rely only on *mass* concentrations and mass mixing ratios of organic and inorganic components, a quantitative description is obtained with respect to all droplet components, including the chemically unresolved NAFA." was removed as it has been clarified already in Section 2.2 / version6.
5. p.12 l.3–4: The sentence "This allows us to compare features of the different surfactant representations also in terms of predicted droplet properties for continuous variation in dry particle compositions." was deleted to reduce amount of text.

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