Response to Reviewer 1:

The technical note summarizes a set of interesting points to be clarified regarding the role of surface active organic aerosol in cloud activation. In light of several recent works, including those of the authors, this topic is very timely and their call for a discussion on the topic is commendable. While it is useful on occasion to summarize the knowledge and open questions in the field, my main concern is that the note brings very little new to the table. Most or all of the points have been made previously, but little references or perspective is given to the substantial body of work already existing on the subject.

We thank the reviewer for his or her comments. As a technical note, the intention of this work is to clarify a key technical point that is often obscured – namely that the evolution of surface tension, in addition to its absolute value at any given droplet size, is an important factor in regulating the activation of CCN. We acknowledge that the theory behind this is established, but it is only in recent experimental efforts that direct observations of modification to Kohler curves have been possible. In these works, the evolving surface tension is shown to change the size of the activating particles, with activation occurring at much larger wet diameters. However, the effect on the activation efficiency (through S_{crit}) is more subtle and can easily be missed when performing typical CCNC experiments. Thus, we aim to clarify why surface tension affects Kohler curves in this manner, and to convey the situations where surface tension effects might be notable and detectable using standard CCN instrumentation. We do not seek to provide a complete or exhaustive review of the literature in the very broad science of CCN activation, instead our focus is on two main points:

1. The evolution of surface tension is the main driver for changes in CCN activation relative to assumptions of fixed surface tension.

2. Current models struggle to explain and predict experimentally observed data across a wide range of parameter space (size, organic fraction and inorganic composition), but experiments can be performed that clearly reveal surface effects which are needed to help to drive the development of new theories and practical, predictive models of CCN growth and activation by the community.

p.2 l. 36-38: "In this note, we focus on the role of surface tension, and discuss the limitations of current approximations in light of recently published works that reveal how it is primarily the evolution of surface tension that impacts the activation process." Only two papers are discussed in detail, the works of Ruehl et al. (2016) and Ovadnevaite et al. (2017). The discussion is not sufficiently substantiated independently of these works.

To our knowledge, it is only in recent papers that experimental observations have been able to corroborate the assertion that surface tension influences hygroscopic growth and CCN activation in organic and mixed inorganic-organic aerosol (Forestieri et al., 2018; Ruehl et al., 2016). These recent studies have done this via direct measurements of droplet size at known saturation ratios (i.e Kohler curves) that show the shape of the curve as activation is approached. While much previous work has discussed the role of surface tension, as noted in our manuscript, there remain only very few studies that directly measure the effects. We wish to emphasize that now the goal is to find a model description to best describe the data over all observable space, based on established physical parameters, rather than fitting an empirical or semi-empirical model to individual datasets. This is challenging, as in many cases surface tension effects are obscured by the way data is presented or analyzed. Indeed, we show that the common practice of showing S_{crit} versus D_{dry} is not effective at highlighting differences that may be attributed to a variable surface tension, due primarily to the larger role that the particle size has in the Kohler equation.

p.3 l.72-75: Effects of inorganic co-solutes is discussed by e.g. Svenningsson et al. (2006), Prisle et al. (2010,2011), Frosch et al. (2011), Kristensen et al. (2014), and Hansen et al. (2015). Effects of dissolution is discussed by e.g. Shulman et al. (1996) and Bilde and Svenningsson (2004).

We thank the reviewer for their recommended additional literature to include in our work, and these have been added to this discussion, indicated below. We acknowledge that there are significant bodies of work outside of those cited in our Technical Note, though we have chosen to avoid a comprehensive review of the field in light of the focus of the manuscript.

"Furthermore, surface partitioning may be influenced by non-surface active components in the system, such as the presence of inorganic material and co-solutes (Asa-Awuku et al., 2008; Boyer et al., 2016; Boyer and Dutcher, 2017; Frosch et al., 2011; Petters and Petters, 2016; Prisle et al., 2011; Svenningsson et al., 2006; Wang et al., 2014). Other factors that have been shown to influence the shape of Köhler curves are: (1) solute dissolution, encompassing both water-solubility and solubility kinetics (Asa-Awuku and Nenes, 2007; Bilde and Svenningsson, 2017; McFiggans et al., 2006; Petters and Kreidenweis, 2008; Shulman et al., 1996), (2) liquid–liquid phase separation (i.e. limited liquid–liquid solubility) (Rastak et al., 2017; Renbaum-Wolff et al., 2016), and (3) the dynamic condensation (or gas–particle partitioning) of organic vapors (Topping et al., 2013; Topping and McFiggans, 2012) (Topping et al., 2013; Topping and McFiggans, 2012).

p.4. l.81: ". . .there are many observations that cannot be explained in such simple terms". Please be specific, which observations cannot be explained and what is the argument that they are unexplained.

The studies cited apply κ-Köhler theory without fully considering the potential influence of surface tension. Collins et al., 2016 note that the method of sea-spray production from bubble bursting likely leads to aerosol more highly concentrated in surface active species. Good et al., 2010 suggest surface tension as a potential source of the deviation in their CCN concentrations. Yakobi-Hancock et al., 2014 briefly discuss data at high organic fraction that shows a much higher κ_{org} than would be expected (albeit with some large uncertainty). These papers demonstrate the conditions where surface tension effects are likely to be significant – the presence of organic molecules with rather low water-solubility present in relatively high concentrations in small particles, as concluded in our manuscript. Thus, these observations cannot be fully explained without considering surface effects. We have modified our language to better reflect the intended meaning:

"While measured cloud droplet number concentrations in the atmosphere have been explained in several cases with simple parameterizations that neglect dynamic surface effects (Nguyen et al., 2017; Petters et al., 2016), there are many observations that are not **fully** explained in such simple terms **and in those cases a substantial population of CCN may exhibit behavior characteristic of surface effects** (Collins et al., 2016; Good et al., 2010; Ovadnevaite et al., 2011; Yakobi-Hancock et al., 2014)"

p. 5-6 and Fig. 1(A): A substantial part of the manuscript is devoted to explaining basic Köhler theory, as done by many authors previously, including basic textbook material. The presentation could benefit from a similarly detailed presentation of the surface tension and partitioning models used.

We carefully state the factors that go into the Köhler equations in order to be thorough and precise in our message. Without fully describing the basic equations, it can be hard to see how water activity and the Kelvin effect affect the results, and how these must be considered separately. A detailed description of the partitioning models of Ruehl et al. (2016) and Ovadnevaite et al. (2017) can be found in their respective manuscripts. Additional information about the AIOMFAC-based models was added to the manuscript on line 236 (line numbers of original manuscript); see our reply to referee #2. However, it is clear that a complete, accurate and predictive description of CCN activation applicable in the general case is not yet available. Rather, our intention is to promote additional laboratory studies and analysis to identify more cases where surface tension has real and measurable effects, in an effort to gain the insight required for producing a predictive theory that captures the full complexity of CCN activation. Thus, we take a step back and focus on the fundamentals of Köhler theory that necessitate the development of the partitioning / surface tension models.

p.7 l. 171-72: "This also seemingly supports previous assertions that surface tension does not impact activation, since it is generally argued that at the point of activation the droplet is sufficiently dilute and essentially exhibits a surface tension like pure water." Please reference a sufficient amount of such previous assertions to support the claim of a general argument.

Earlier in the text, we discuss the references that point to this assertion (lines 44+) and we have amended the text to refer the reader back to this section:

"Traditionally, however, surface tension has been reduced to a fixed term in the Köhler equation (Abdul-Razzak and Ghan, 2000; Facchini et al., 2000; Petters and Kreidenweis, 2007) and is usually given a temperature-independent value equal to that of pure water at 25 °C. This is because for any decrease in surface tension due to bulk–surface partitioning and surface adsorption, it is assumed that there is an increase in the solution water activity because adsorbed material, previously acting as a hygroscopic solute, is removed from the droplet (bulk) solution (Fuentes et al., 2011; Prisle et al., 2008; Sorjamaa et al., 2004). Thus, the effects approximately cancel out in the calculation of a droplet's equilibrium saturation ratio via the Köhler equation and so are often neglected. Furthermore, it has been shown in some cases that there is insufficient material in a droplet at the sizes approaching activation to sustain a surface tension depression (Asa-Awuku et al., 2009; Prisle et al., 2010)."

p.8 l.180: ". . . knowing the surface tension only at the point of activation is insufficient to determine the critical properties at activation. . ." Please provide references.

We have rephrased this statement to clarify our meaning, as this reflects an important point. The text here now reads:

"Clearly, an evolving surface tension prior to activation can matter in such systems and, consequently, knowing the surface tension only at the point of activation is in a general case insufficient for determining the critical properties at activation (absent any droplet size measurement), because the position of the maximum in the Köhler curve and, thus, the droplet size at activation, will depend on the trajectory of surface tension evolution. Moreover, knowing the surface tension at the activation point only, may not allow for an accurate prediction of whether a droplet of given dry diameter will activate at a given environmental supersaturation (compare the green curve with the *iso-σ* curve of 72 mN m^{-1} in Fig. 1B, both having the same surface tension at their points of CCN activation, yet different critical supersaturations and wet diameters). Similar conclusions have been drawn previously (e.g. Prisle et al., 2008), although the measurements by Ruehl et al. (Ruehl et al., 2016) were the first to verify this experimentally."

p.11 l.258-64: "This predicted size effect indicates that it is not generally valid to assume that all activating CCN will have a surface tension equivalent to or close to that of pure water –nor is it appropriate to use a single measurement of the surface tension of a multicomponent CCN of known dry composition at its activation size (only) to determine its Köhler curve. Furthermore, these model predictions also suggest that measurements of the surface tension of larger CCN particles (e.g. > 150 nm dry diameter) may not allow for conclusions about the surface tension of much smaller CCN, e.g. of 50 nm dry diameter." These points have certainly been made by other studies than the one specifically

described, including those mentioned above, and Wittbom et al. (2018). A broader perspective should be provided.

Studies that do not explicit account for surface partitioning, such as Wittbom et al., indicate there is a size-dependence to their values of κ, and implying to us that there might be surface tension effects at play. The studies of e.g. Prisle et al. (2008), Prisle et al. (2010) and Sorjamaa et al. (2004), now cited in the text at this point, discuss size-dependent surface tension but do not appear to show clear deviations from an assumption that surface tension is size-independent. Indeed, Sorjamaa et al. conclude the opposite of the observations reported here – that surface effects become more significant with larger particles. As we show in Figure 2, we note the opposite, that smaller particles of the same composition are more CCN active and thus suggests greater surface tension effects. We have now cited additional papers in this context that discuss size dependencies relating to surface partitioning.

p.12 l. 292-92: "…in contrast to other studies that allow both coated particle size and organic volume fraction to vary simultaneously." Although in many studies particles are produced by other methods than coating (e.g. nebulization), again many other works have indeed recognized the importance of independently varying the particle size and organic fraction, for studying the effects of organic surface activity and mixing effects, including those listed above.

We acknowledge that other studies have performed measurements in this manner and have now included references to Prisle et al. (2010) and Wittbom et al. (2018). Many studies do however only show data where f_org is varied in conjunction with D_dry, which we argue conceals subtle surface effects that might influence the system.

p.13 l.310-12: "One could ignore the physical meaning of K and simply use it as an all-encompassing parameter to describe activation efficiency." This was already done by several previous studies, e.g. Kristensen et al. (2014) and Hansen et al. (2015). I do understand that the authors caution against it, but see also my points below. p.13 l.312-13: "In this case, the generality of the parameter to interpret observations in different conditions is lost." Please explain what is meant by this statement, and how that would not be the case by separating out surface tension from the K parameter. Please give references to previous work debating this, as well as to the original work of Petters and Kreidenweis (2007) and following articles to support why this is not the proper way to interpret their presented framework.

When comparing the formulation of κ-Köhler theory by Petters and Kreidenweis (2007) to the complete Köhler theory, the κ parameter is equal to the ratio of the molar volume of water to the molar volume of a non-electrolytic solute for an ideal solution – therefore representing a simplified model for water activity. Thus, deviations from this exact value can be attributed to non-ideality. Water activity, however, is a function of the bulk concentration, and thus should be decoupled from surface effects (and be size invariant). By using κ to account for both water activity and surface tension, a size dependence is introduced due to bulk–surface partitioning and surface-to-volume ratio, and thus its generality is lost. In the general Köhler equation, water activity is a factor distinct from the Kelvin factor and therefore one distinguishes between surface tension effects and bulk solution non-ideality (which relates to hygroscopicity also at RH < 100 %). By using κ as an adjustable fit-parameter, one may be able to fit experimental data, but by doing so, the retrieved κ will be system-specific and size-specific if the actual surface tension of the droplets varied with size. Such system- and size-specific fitted models will not serve the purpose of establishing a predictive theory and model. This is why we caution against it.

p.13 l.318-19: "… a specific suberic acid hygroscopicity alone cannot explain the observations across a range of particle sizes and compositions" That was also found for other well-defined organic aerosol by

e.g. Kristensen et al. (2014), Hansen et al. (2015), and Wittbom et al. (2018). Indications of similar relations have been seen for ambient aerosol by e.g. Hong et al. (2014,2015).

The mentioned studies report agreement when looking at critical supersaturation vs D_{dry} (D_{coated} in our manuscript). Indeed, Kristensen et al. conclude that a fixed surface tension of water and a fitted κ value for the organic fraction gives best agreement. Hansen et al. are not definitive in their conclusions of a size dependent κ, although they do indicate that smaller particles exhibit a greater surface tension reduction, and the focus of Wittbom et al. is on solubility, which may show different size dependencies than surface tension and is thus not directly relevant for the discussion here. The data and choice of coordinates we report in Figure 2 is the most clear demonstration that a single value of κ cannot reproduce the data for this system across different sizes. Decoupling size from composition allows for a more rigorous assessment of the effectiveness of a model in account for each parameter. D_{dry} is not a sensitive metric for observing deviations due to surface tension because both size and composition vary, and their effect on the extent of surface tension effects is opposite. That is to say, as D_{dry} gets smaller (likely to increase role of surface tension), the organic fraction decreases (likely to decrease role of surface tension). Thus, the influence of surface tension is masked by the manner in which the data is presented.

p.15 l.349-50: “. . .all organic material is assumed to reside in a water-free organic shell-phase (an organic film) at the surface of the aqueous droplet.” This assumption was also used by e.g. Prisle et al. (2011).

This assumption, as we discuss, is the most simple to apply, and yields the best results for the sample case discussed. Given that it is not well-supported by the applied partitioning theory for the case of suberic acid, it is interesting that this is the case and suggests we have a long way to go to quantitatively understand what is happening during the CCN activation process. In Prisle et al. (2011), this assumption is applied for the case of “classic” surfactants for which conceptually such an assumption might seem more appropriate. In our case, this assumption still yields good results, despite the molecules not being true surfactants. In general, this organic film assumption represents a limiting case, and in reality a balance between surface partitioning and water activity suppression should explain the results. We have added the following sentence to acknowledge these previous studies:

“This observation is consistent with the results of (Prisle et al., 2011) who applied a similar simple model to droplets containing ionic surfactants and hints at a significant suppression of surface tension by suberic acid, which is likely highly enriched at the droplet surface”

p.15 l.349-50: “. . .neither of the models fully captures the observed behavior at all forg and size regimes.” Previous studies have made similar conclusions for other aerosol and other models, please bring these into perspective to present a broader perspective of the issue.

[The referee refers to line 359] The discussion in this section of the manuscript concerns the system and models shown in Fig. 2. To discuss previous literature which makes similar conclusions for other aerosol systems – yet not presented in terms of organic volume fraction at constant size cases – does, in our opinion, not add to the purpose of the discussion at this point in the article.

p.17 l.399-400: “Surface tension effects can lead to significant differences from classic, hygroscopicity mixing rule mechanisms for CCN activation.” This was also seen by Kristensen et al. (2014) and Hansen et al. (2015), among others.

We have added additional citations here to refer readers to the works the reviewer suggests.

p.30: For example Shulman et al. (1996), Sorjamaa et al. (2004), and Prisle et al. (2008) present similar Köhler curves. Please discuss Fig. A2 in context of previous results.

This type of Köhler curve is produced when additional factors that determine the water activity or surface tension vary with the changing particle size. Solubility limitations and surface tension suppression both produce plots that may exhibit discontinuities. The point of Fig. A1 and associated text in the manuscript is to illustrate the different outcomes of the employed AIOMFAC-based model variants for a specific case of the aqueous suberic acid + ammonium sulfate system including accounting for liquid–liquid solubility limitations. We do agree with the referee that Köhler curves similar in shape have been produced by other models for other systems in the past, including in the work by Shulman et al. (1996) but we note also that the shapes of such variable-σ Köhler curves were only recently verified experimentally.

The most significant novelty of this work lies in the measurements presented in Fig. 3, but these results lack a comprehensive discussion.

These results were included to highlight the other factors that influence observations and demonstrate that co-solute effects are important to consider. These observations must also be accounted for in any predictive overall model, and are thus included to illustrate the need for a comprehensive theory applicable over the relevant parameter space.

Significantly more novel content should be added to the work before publication. For example, no explanation is given for the variation between the salt seeds and no modeling is done to provide interpretation beyond general speculation. Would it not be possible and facilitating to the discussion to make model predictions using exactly the outlined framework, for these aerosol? CCN activation experiments could be made with the systematic variation in particle size and organic fraction which this technical note specifically calls for. How are the impacts on water activity from the different salts treated in the model? Could intrinsic salt hygroscopicity/solubility explain the variation with mass fraction, and if not, why? More generally, a discussion could be added on the atmospheric/organic aerosol process relevance of suberic acid and mixtures with each of the salts.

As a technical note focused on conveying a single point, the role of evolving surface tension on CCN activation, a broader discussion is beyond the scope of this note. Moreover, we emphasize that the goal for showing the data of Fig. 3 is not in fitting a specific (simple or sophisticated) CCN activation model to the data presented in Fig. 3; rather, the point is made that additional complexity is observed with respect to organic–inorganic interactions stemming from different types of solute species. We agree that these data are particularly interesting, and hope further studies will be able to learn from what we present here and offer more tangible theoretical frameworks that allow the relevant physical parameters to be accurately included.

For the model part, I commend the effort to use a more general activity model for calculating the Köhler curves. This is indeed one of the major sources of discussion related to identifying surface tension effects in Köhler theory. However, the use data presented in Table 1 is not sufficiently justified. For example, why was the 20 C values used? What is the basis for assuming similar surface tension based on structural similarity? For other compounds, small changes in molecular length can lead to greatly enhanced surface activity. How did Riipinen et al. make the determination of the pure compound value? How is pure ammonium sulfate (a solid at 20 C) surface tension justified? How is the minimum shell thickness estimated? .

Adipic acid and suberic acid are the closest in size of the dicarboxylic acid series, and both contain even numbers of carbons. It is indeed true that smaller changes can result in large differences of surface tension, but this is typical seen when going from even to odd, and that adjacent even or odd compounds are more similar (Ruehl and Wilson, 2014). The tabulated value for suberic acid is that estimated for the pure liquid (subcooled) component; its value is likely similar to that of pure liquid (subcooled) adipic acid and other dicarboxylic acids. Adipic acid's pure value was determined theoretically using the Macleod-Sudgen method, as described in Riipinen et al. A pure component surface tension is a physicochemical property that is distinct from a molecule's surface affinity in a solution droplet (however, when such a substance contributes a substantial area fraction of the surface, it's surface tension value will affect that of the droplet). A temperature of 20˚C was used because this was the ambient temperature in which the experiments were conducted. The ammonium sulfate was not considered to influence surface tension at dilute aqueous conditions, as noted in the footnote to Table 1. We have amended the text in the table to state "surface tension of aqueous AS (at T)". The minimum shell thickness is one of the assumptions applied in the predictive AIOMFAC-based model and is established based on the approximate size of the molecules and related monolayer thickness.

What would be the impact on Köhler curves using more mixture specific input data? Can the authors rule out that any of the effects described are not caused by solution non-ideality and misrepresentation of the experimental system by use of incompatible thermodynamic data? It would strengthen the arguments significantly to use accurate reference input data if such may be obtained from a thorough literature search, or from performing new measurements for the specific systems in question. The lack of proper input data for different Köhler models is a major limitation of obtaining a comprehensive molecular framework, as called for in this technical note – this would be one of my first additions to the discussion.

We agree with the reviewer that any model should use input data which are directly measured rather than fit to the experimental data in question. We are not sure what misrepresentation the reviewer might be referring to – the main conclusion of the paper, as supported by the experimental results, is that we do not have a correct model, and perhaps lack the correct inputs or physicochemical details to fully understand what is happening. However, we do consider bulk phase non-ideality in the models explicitly, including organic–inorganic interactions in the AIOMFAC model, aspects often ignored in other models. We are confident that the thermodynamic data used for model inputs are correct (or reasonable estimates where direct measurements are lacking). The application of a spectrum of models in this work is to demonstrate that surface effects can reasonably explain and constrain the observations, but that a robust, accurate and fully predictive model for such coupled hygroscopicity and surface tension effects is yet to be developed.

The discussion about discontinuities in the activation curves is very interesting. It would be useful to see Fig. 1(B) developed for somewhat more realistic conditions. Specifically, do similar discontinuities persist in Köhler curves when concentration dependent partitioning is taken into account? What are the relation between the curves in Fig. 1(B) and A2? Why do they look different?

Figure 1(B) is a schematic using exaggerated surface tension dependencies to highlight the differences that may be encountered based on different surface tension evolutions. Those shown in A2 result from the AIOMFAC-based model variants for the suberic acid + AS system, as described in the manuscript. Not all possible schematic surface tension evolutions are exhibited by a single system. Discontinuities in Köhler curves, similar to the schematic in Fig. 1B, have been observed e.g. by Ruehl et al. (2016) for droplets containing ammonium sulfate and various dicarboxylic acids. Those observations and discontinuities were reproduced by a (fitted) compressed film model of CCN activation.

The present technical note draws primarily on the previous work of Ruehl et al. (2014,2016). It should be made clearer which results are summarized from there, and which are new for this work. The

presentation and arguments would benefit greatly from an independent presentation of the model framework and main assumptions used. In particular, it is not entirely clear what partitioning framework is used and how the surface composition is actually evaluated. It is not clear how mutually different the employed frameworks are, that is, how wide a range of possible representations of the aerosol are mapped with the three different models used. As the majority of previous work uses a Gibbs-based partitioning model, would it not make sense to include such calculations in the comparison? The results in Fig. A2 could be discussed in greater depth, as could the statement "... the simplified organic film model provides the best description of these experimental data" p. 16 l.374. Why was the "best framework" not verified by e.g. measuring the droplets size at various equilibrated RH?

The main intention of this paper is not to present a "best" model in the sense of a recommendation to the community. The main goal is to show that current models are insufficient in capturing the details and the dynamics across a range of parameter space relevant to CCN activation. While different from classical Szyszkowski-Langmuir isotherm model for bulk-surface partitioning and surface tension, the compressed film model by Ruehl et al. (2016) employed in this work is also a model that includes a thermodynamically consistent isotherm model for relating surface composition to bulk concentration. A more detailed description of the models is therefore unwarranted.

Response to Reviewer 2:

While it is not entirely clear to me why this is being framed as a "technical note," and not just a paper, I find the results to be generally interesting. There is effectively a very long introduction in which the authors lament that others continue to neglect the role that surface tension can play, followed by some interesting discussion of some new experiments. I suggest that the discussion about the new experiments is expanded.

We thank the reviewer for his/her time in reviewing our manuscript. We present this work as a technical note in order to convey the key point to the work – that it is the evolution of surface tension, in addition to the absolute value at any given droplet size, that is important in regulating the activation of CCN. The introduction serves to ensure the reader has sufficient context in order to appropriately apply and considerer surface tension effects when assessing CCN data.

L150: I find the terminology "schematic dependences" to be a bit unclear. It would be good to see this explained a bit further. Do these come from anywhere in particular, or are they totally made up? What sort of cases are they meant to illustrate, i.e. why these three?

These are schematic in the sense that they do not conform to the behavior of any particular solute/solvent system. However, they represent the types of dependencies that are encountered and the resulting implications on the Kohler curves. The text now reads:

"Distinct schematic dependences of the surface tension on the droplet size, representative of the types of dependence that might be encountered in real aerosol, are imposed for the purpose of illustration, shown in the lower panel of Figure 1B"

L170: It is not clear to me how the statement that "This. . .supports assertions that surface tension does not impact activation. . ." follows from the previous sentence. In the examples, the activation diameter for all three non-constant surface tension curves is lower than that obtained assuming a constant surface tension equal to that of pure water. In fact, the authors go on to say just this. So, it would seem that the activation diameter is impacted. It would be helpful if the authors could clarify their particular point here.

Figure 1B shows the opposite of what is being asserted by the reviewer – each of the curves associated with a variable surface tension exhibits an activation diameter that is larger (not lower) than the constant surface tension curve. While surface tension at the point of activation may be equal to that of pure water, the simulations here indicate that the point of activation is modified by the evolution of the surface tension. The point in the mentioned sentence on L170 is that in most CCN measurements, only the activation supersaturation is measured for a given dry size, but not the activation size nor the surface tension. Thus, one might assume that the surface tension at the activation point is equal to that of pure water, which may frequently be the case. However, as the examples in Fig. 1B show, assuming that the surface tension is constantly that of pure water prior to reaching those dilute conditions and using a determined hygroscopicity parameter to predict the Köhler curve and CCN activation point would lead to a substantially different critical supersaturation and activation diameter (that of the peak in the 72 mN/m Köhler curve). Or in case of a measurement of critical supersaturation in order to determine a particle's true hygroscopicity parameter at CCN activation, an incorrect parameter would be determined (one that would accidentally combine surface tension evolution effects and actual hygroscopicity in a non-trivial and incorrect way).

L182: The "discontinuity" that the authors refer to here is not entirely clear to me. Do the authors mean that each of the three variable curves shown suddenly changes relatively to assuming a constant surface

tension of 30 mN/m? This is not clear from the words, as the discontinuity does not occur "at its minimum surface tension" but instead when there is a (in the model used here) discontinuous increase in the minimum surface tension.

The term "discontinuity" was used because the gradient of the Kohler curve changes discontinuously when realistic surface tension profiles are included. To better reflect the changes in the function itself, we now refer to these as abrupt changes in the text. The "second discontinuity" comments have been omitted in the revised manuscript as they distract from the more important facets of the discussion.

L235: It would be helpful if the "relatively simple, phase composition- and morphology specific surface tension model" were described here, in brief. If I understand correctly, a linear mixing rule is used.

At this line in the manuscript, we now add the following brief description of the AIOMFAC-based model and mixing rules for surface tension used:

"A detailed description of this AIOMFAC-based model, its variants and sensitivities to model parameters and assumptions is given in the supplementary information of Ovadnevaite et al (2017). Briefly, the equilibrium gas–particle and liquid–liquid partitioning model is used to predict the phases and their compositions for a bulk mixture "particle", here of known dry composition, at given RH and temperature. For other applications with given total gas + particle input concentrations, the equilibrium condensed-phase concentrations can be computed as a function of RH (accounting for partitioning of semivolatiles). Assuming spherical particles of a certain dry diameter with a core-shell morphology of liquid phases in the case of LLPS, density information from all constituents is used to compute volume contributions and the size of the particle at elevated RH. In addition, the surface tension of each individual liquid phase is computed as a volume-fraction-weighted mean of the pure-component surface tension values. In the case of LLPS, the surface coverage of the organic-rich shell phase is evaluated by considering that it must be greater than or equal to a minimum film thickness (monolayer as a lower limit); this determines whether complete or partial surface coverage applies for a certain wet diameter. The effective surface tension of the whole particle is then computed as the surface-area-weighted mean of the surface tensions of contributing phases. This way the surface tension evolves in a physically reasonable manner as a droplet grows, including the possibility for abrupt transitions from a low surface tension, established due to full organic droplet coverage under LLPS, to partial organic film coverage after monolayer film break-up, and further to complete dissolution of organics in the aqueous inorganic-rich phase (single aqueous phase). This equilibrium model is here referred to as AIOMFAC-EQUIL. We also employed two AIOMFAC-CLLPS model variants, in which the organic constituents are assumed to reside constantly in a separate phase from ammonium sulfate (complete LLPS, an organic film), either with or without water present in that phase, discussed in Section 4."

L235: It would also be helpful if the authors were to clarify whether the model predicted the surface activation effect completely independent of the observations, or whether some amount of model tuning was included (perhaps associated with exactly what species were chosen to represent the organic phase).

In the study by Ovadnevaite et al. (2017) a predictive model based on AIOMFAC was employed. The predicted surface tension evolution by that model is a result of the calculations when liquid–liquid phase separation is included; no model tuning was performed concerning the model physics. However, the reviewer is correct that the selection of surrogate species, used to represent a particular "ambient" organic-inorganic aerosol system, will affect the predictions. In the case of the Ovadnevaite et al. study, the selection of surrogate species and their concentrations were constrained by available observations on the chemical composition of the aerosols. Obviously, no molecular-level composition information was available and as such, a range of options may be considered. Hence, the choice of system components and compositions may affect predicted CCN properties, however, beyond that, the surface tension and particle size as a function of water activity was purely a result of the computations. Extensive results and sensitivity calculations on composition and physical parameters are documented in the SI of Ovadnevaite et al. (2017) and not of relevance for the discussion in this technical note.

Concerning the modelling results described in this work, the organic to salt ratio, hence dry composition, is known and no tuning of input parameters was performed. Instead, we rely on physical parameters established independently of this work to assign feasible input parameters and compare with our experimental observations. Fitting a model to these data would not yield insight into whether our understanding of several key processes is complete. Indeed, our conclusions are that we do not have an accurate model description of the process over a range in dry particle sizes, and so we are still some way off from a predictive framework.

L244: I suggest that the authors modify the sentence ending "process" to say "process, for these systems." It is not clear that this is the case for all systems. If it were, we might expect to see a lack of closure more generally in ambient measurements.

We have amended the manuscript to reflect this clause.

L251: What is stated does not appear to be the case for the example shown in Fig. S3.7.4 in the Ovadnevaite paper.

The figure panels corresponding to the equilibrium AIOMFAC model with LLPS in that study show activation occurring at the point when surface tension returns to the value for pure water (Fig. S3.7.4a by Ovadnevaite et al.). This is in contrast, for example, to the prediction by the same model for the same system and conditions by dry particles of 41 nm diameter, which is why we point to a size dependence when the surface tension at the activation point is discussed. Other models, including the organic film variant, predict a reduced surface tension at the activation point even for larger dry diameter, yet also that variant points to a size dependence of the surface tension at activation.

L305: I do not find it clear what the authors mean when they state that the compressed film model "more closely predict[s] the observations." More closely than what? The simple model assuming a constant kappa_org = 0.35 seems to do quite well. I do get that the authors are working to say that kappa_org = 0.35 is not the correct answer and thus the good agreement is not for the right reason. Yet this discussion requires clarification.

We agree this is confusing, and that statement has been removed, replaced with:

"The compressed film model decouples the water activity component from the surface tension component, and thus should better represent the physical processes at work. However, the agreement for all these models breaks down further when looking at different sized particles."

as a concluding remark prior to our discussion of size dependencies.

L316: Is the compressed film model here simply inadequate, even with determination of new parameters? Or can it work if it were returned to this dataset? If the latter, this would give some indication of how uncertainty in the derived parameters for the model impacts subsequent calculations.

In the current compressed film model framework, no combination of parameters was able to reproduce the trends for all size regimes considered. Some imposed additional size dependencies on the input parameters might produce good agreement, but at that point the model becomes a multivariable fit rather than a predictive physical framework.

L328: This is only true for the smallest particles.

This is stated on line 327 referring to the 40 nm particles.

L330: I am not seeing entirely what information is lost by choice of procedure or data representation. Both ways of representing the data seem to drive one to similar conclusions: for a given representation the assumption of a constant kappa_org can allow for model-measurement agreement, but the kappa_org values are not necessarily realistic. I do not understand why the authors couldn't similarly apply the models shown in Fig. 2A/B to the data in Fig. 2C? There need not be loss of information.

We are trying to show in these figures that by including size and composition in a single axis (as in the case of Figure 2C with D_{coated}), it becomes much harder to discern whether the model is doing a good job or not. The smallest size particles, which show the biggest surface effects when predominantly organic in nature, are at low organic volume fractions in this representation (fixed inorganic seed size), and the larger particles that do contain more organic show less surface sensitivity. Hence, for the same data, it might be reasonably concluded that a fixed value of kappa_org results in good agreement across the dataset, when in reality it is not fully capturing all the dependencies. There is no true loss of data, and we have amended our comments in the manuscript to better reflect our meaning.

"Thus, the choice of experimental procedure or data presentation can impact the interpretation of experimental observations and we caution care when presenting such data. When composition and particle size are coupled in D_{coated}, the sensitivity to surface tension effects is diminished, as smaller particles will contain a lower volume fraction of organic material"

L348: It is not clear to me how these are AIOMFAC calculations any longer, if the organic and salt are forced into separate phases. Does one even need AIOMFAC to do this?

The non-ideal mixing among the compounds within each phase is still treated with AIOMFAC, necessary to determine the water content as a function of RH (of the inorganic core phase or of both phases, depending on the model variant). The AIOMFAC-CLLPS (w/ org film) model is a simplified implementation of a possible, yet extreme case of phase partitioning and serves as a starting point. We are not presenting this model as the answer; indeed more questions are raised by the success of such a simple implementation in predicting surface effects in this case study.

L361: How is it that the essentially made up model (assuming a complete surface film) does better than the model that explicitly accounts for the system thermodynamics? Is this just saying that the thermodynamic model is wrong (e.g. bad parameterization or parameterization used outside the RH range where it is valid)? Or is there perhaps some kinetic effect that must be accounted for? The discussion that comes a few sentences later seems to suggest perhaps the former. But, some additional and more explicit discussion is necessary, rather than a statement (line 375) that this finding is "intriguing".

This is indeed an interesting point, and the answer is we don't know. Clearly the more rigorous thermodynamic models miss something, such as how interfacial energies between liquid phases (not considered explicitly) might drive the system towards enrichment of the organic phase. The AIOMFAC-CLLPS (w/ org film) presented here is a limiting case in this treatment of the system and is an educated first guess at the solution. Kinetic effects may be in play, but typically these would make activation harder (dissolution kinetics, water uptake kinetics etc.).

Minor Comments:

Fig. 1: It would be good to change from the red/green color scheme to one that is more friendly to color blind people.

Done.

Technical Note: The Role of Evolving Surface Tension in the Formation of Cloud Droplets

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Abstract. The role of surface tension (σ) in cloud droplet activation has long been ambiguous. Recent studies have reported observations attributed to the effects of an evolving surface tension in the activation process. However, adoption of a surface-mediated activation mechanism has been slow and many studies continue to neglect the composition-dependence of aerosol/droplet surface tension, using instead a value equal to the surface tension of pure water (σ_w). In this technical note, we clearly describe the fundamental role of surface tension in the activation of multicomponent aerosol particles into cloud droplets. It is demonstrated that the effects of surface tension in the activation process depend primarily on the evolution of surface tension with droplet size, typically varying in the range $0.5\sigma_w \lesssim \sigma \leq \sigma_w$ due to the partitioning of organic species with a high surface affinity. We go on to report some recent laboratory observations that exhibit behavior that may be associated with surface tension effects, and propose a measurement coordinate that will allow surface tension effects to be better identified using standard atmospheric measurement techniques. ~~However~~Unfortunately, interpreting observations using theory based on surface film and liquid-liquid phase separation models remains a challenge. Our findings highlight the need for experimental measurements that better reveal the role of composition-dependent surface tensions, critical for advancing predictive theories and parameterizations of cloud droplet activation.

1 Introduction

The formation of a cloud involves a complex series of steps as nanometer sized aerosol particles, termed cloud condensation nuclei (CCN), grow by condensation of water vapor to become supermicron-sized cloud droplets, in a process known as CCN activation. Activation depends on physicochemical properties of the aerosol, such as hygroscopicity and surface tension, as well as atmospheric conditions, such as temperature and humidity. To accurately predict cloud formation and properties, these factors must be included in modelling schemes. However, due to computational limitations, approximations and simplifications are needed, which often obscures the underlying physics and may limit the accuracy of predictions. A key challenge is in the development of a simple model that captures the basic processes involved in CCN activation, while allowing complicating factors such as surface tension variability, solubility and phase separation to be included in a physically representative manner. In this note, we focus on the role of surface tension, and discuss the limitations of current approximations in light of recently published works that reveal how it is primarily the evolution of surface tension that impacts the activation process.

In recent publications, the role of surface tension in the activation of aerosol particles to cloud droplets has been reexamined (Forestieri et al., 2018; Ovadnevaite et al., 2017; Ruehl et al., 2016) . These studies show that the evolution of surface tension can have a large effect during the activation process compared to when surface tension is assumed to be a static parameter. It is well established that surface tension is a factor in activation, and that dissolved species can suppress surface tension (Li et al., 1998). Traditionally, however, surface tension has been reduced to a fixed term in the Köhler equation (Abdul-Razzak and Ghan, 2000; Facchini et al., 2000; Petters and Kreidenweis, 2007) and is usually given a temperature-independent value equal to that of pure water at 25 °C. This is because for any decrease in surface tension due to bulk–surface partitioning and surface adsorption, it is assumed that there is an increase in the solution water activity because adsorbed material, previously acting as a hygroscopic solute, is removed from the droplet (bulk) solution (Fuentes et al., 2011; Prisle et al., 2008; Sorjamaa et al., 2004). Thus, the effects approximately cancel out in the calculation of a droplet's equilibrium saturation ratio via the Köhler equation and so are often neglected. Furthermore, it has been shown in some cases that there is insufficient material in a droplet at the sizes approaching activation to sustain a surface tension depression (Asa-Awuku et al., 2009; Prisle et al., 2010). The lack of experimental evidence to the contrary has led to the adoption of these assumptions in popular single-parameter~~s~~ models, such as κ-Köhler theory, that reduce the complexity of the activation process (Petters and Kreidenweis, 2007). These parameterizations provide a compact and useful means of relating key observables, such as the critical supersaturation and activation diameter, to hygroscopicity and allow a general comparison between systems with arbitrary compositions. The κ-Köhler framework has also been adapted to account for surface tension effects (Petters and Kreidenweis, 2013). However, a single parameter implementation cannot account for the full effects of an evolving surface tension and, by omitting the microphysical processes associated with bulk–surface partitioning, the presence and magnitudes of any surface effects are often difficult to ascertain.

In the works of Ruehl and coworkers (Ruehl et al., 2016; Ruehl and Wilson, 2014), Forestieri and coworkers (Forestieri et al., 2018) and Ovadnevaite and coworkers (Ovadnevaite et al., 2017), laboratory and observation-based measurements, respectively, combined with a partitioning model have revealed key signatures of surface tension lowering in the activation process due to non-surfactant organic compounds. Notably, that a modification of the Köhler curve can result in lower critical supersaturations and vastly different droplet sizes at activation compared to the expectation when assuming a constant surface tension. Dynamic factors may also play a role, as discussed by Nozière and coworkers (Nozière et al., 2014) who have shown that surface tension can vary over time due to slow changes in the bulk-surface partitioning of material, leading to a time-dependence in the role of surface tension. This may be especially important for droplets that initially contain micelles or oligomers that exhibit slow breakdown kinetics and diffusion. Furthermore, surface partitioning may be influenced by non-surface active components in the system, such as the presence of inorganic material and co-solutes (Asa-Awuku et al., 2008; Boyer et al., 2016; Boyer and Dutcher, 2017; Frosch et al., 2011; Petters and Petters, 2016; Prisle et al., 2011; Svenningsson et al., 2006; Wang et al., 2014). Other factors that have been shown to influence the shape of Köhler curves are: (1)

solute dissolution, encompassing both water-solubility and solubility kinetics (Asa-Awuku and Nenes, 2007; Bilde and Svenningsson, 2017; McFiggans et al., 2006; Petters and Kreidenweis, 2008; Shulman et al., 1996)~~(Asa-Awuku and Nenes, 2007; McFiggans et al., 2006; Petters and Kreidenweis, 2008)~~, (2) liquid–liquid phase separation (i.e. limited liquid–liquid solubility) (Rastak et al., 2017; Renbaum-Wolff et al., 2016), and (3) the dynamic condensation (or gas–particle partitioning) of organic vapors (Topping et al., 2013; Topping and McFiggans, 2012) (Topping et al., 2013; Topping and McFiggans, 2012). While measured cloud droplet number concentrations in the atmosphere have been explained in several cases with simple parameterizations that neglect dynamic surface effects (Nguyen et al., 2017; Petters et al., 2016), there are many observations that ~~cannot be~~are not fully explained in such simple terms and in those cases a substantial population of CCN may exhibit behavior characteristic of surface effects (Collins et al., 2016; Good et al., 2010; Ovadnevaite et al., 2011; Yakobi-Hancock et al., 2014). In order to gain a robust and predictive understanding of CCN activation, a molecular-level theory must be developed and adopted by the atmospheric chemistry community.

In this technical note, we offer a perspective on the role of surface tension in the activation process, drawing on recent studies and interpretations of cloud droplet activation measurements (e.g. (Forestieri et al., 2018; Ovadnevaite et al., 2017; Ruehl et al., 2016; Ruehl and Wilson, 2014). We go on to discuss how surface tension may be considered in the activation process, and finally present some new data highlighting potential indicators of surface tension effects in measurements of critical supersaturation. Our aim is to provide a platform for discussion and help foster a molecular-based interpretation of the role of organic material in the activation of aerosol to cloud droplets.

2 Clarifying how Surface Tension Alters Cloud Droplet Activation

On a fundamental level, the influence of surface tension on droplet activation is straightforward and was discussed in the late 1990’s for aerosol particles containing surfactants (Li et al., 1998). Unfortunately, the simplicity of the role of surface tension in CCN activation has been lost in the complex descriptions of surface and phase-partitioning models, limiting the broader application of the insights gained from recent experimental results. For context, we begin our discussion with Köhler theory (Köhler, 1936), which describes the thermodynamic conditions required for CCN activation based on two contributions that control the equilibrium (saturation) vapor pressure of water above a liquid surface. The classic Köhler equation is often written as (Petters and Kreidenweis, 2007):

$$S_d = \frac{p_{w,d}(\mathrm{D})}{p_w^0} = a_w \exp\left[\frac{4\,M_w\,\sigma}{RT\rho_w \mathrm{D}}\right], \qquad (1)$$

where S_d is the equilibrium saturation ratio of water in the vapor phase surrounding a droplet surface, $p_{w,d}$ (D) is the equilibrium partial pressure of water vapor above a droplet (subscript d) of diameter D and a certain chemical composition, p_w^0 is the pressure of water above a flat, macroscopic surface of pure liquid water at temperature T, a_w is the mole-fraction-based water activity of the droplet solution, M_w is the molecular mass of water, σ is the surface tension of the particle (at air-liquid interface), R is the ideal gas constant, and ρ_w is the density of liquid water at T. The water activity contribution, known as the solute or Raoult effect, describes a lowering of the equilibrium water vapor pressure above a liquid surface due to the presence of dissolved (hygroscopic) species that reduce the water activity to a value below 1. The second contribution, known as the Kelvin effect, describes an increase in the equilibrium water vapor pressure above a microscopic curved surface and is dependent upon the surface area-to-volume ratio of the droplet (a size effect) and the surface tension, i.e. the gas-liquid interfacial energy per unit area of surface. The latter term arises from the energy associated with creating and maintaining a certain surface area and, thus, is reduced when the surface tension is lowered or when the droplet size increases, leading to a smaller surface-to-volume ratio. The magnitude of the Kelvin effect scales with the inverse of the droplet radius and is sometimes referred to as the “curvature effect”. The combined contributions from the Raoult and Kelvin effects in Köhler theory define a thermodynamic barrier to droplet growth. It is important to note that the Köhler equation describes the specific saturation ratio S_d in thermodynamic equilibrium with a certain solution droplet of interest; however, the value of S_d may differ from that of the environmental saturation ratio, S_{env}, present in the air parcel containing the droplet, since S_{env} is established by an interplay of moist thermodynamic processes. The environmental saturation ratio is defined by $S_{\mathrm{env}} = \frac{p_w}{p_w^0}$, where p_w is the partial pressure of water in air at a specific location and time, irrespective of the presence or absence of aerosols and cloud droplets. The global maximum in a Köhler curve marks the point of activation for a certain CCN, as shown in Figure 1A. For conditions of $S_d \leq S_{\mathrm{env}}$, e.g. in a rising, adiabatically expanding air parcel, aqueous CCN equilibrate relatively quickly to their environmental conditions such that $S_d = S_{\mathrm{env}}$ is maintained (stable growth/evaporation). However, when S_{env} exceeds the global maximum in S_d for a certain CCN, such an equilibration becomes unattainable and net condensation of water prevails, leading to so-called unstable condensational growth for as long as $S_{\mathrm{env}} > S_d$ holds (while S_d varies according to the pertaining Köhler curve).

A Köhler curve shows the relationship between the droplet's equilibrium water vapor saturation ratio and the wet droplet size. The wet droplet size, or more specifically the chemical composition (solute concentration), solubility and non-ideal mixing determines the water activity, while the size and surface tension determine the Kelvin effect. Since the solute concentration changes with the droplet size, e.g. during net growth conditions when the environmental saturation ratio in an air parcel increases and water vapor condenses, the water activity term varies accordingly, typically in a non-linear manner. The Kelvin term should also change with droplet size, both due to the changing surface-to-volume ratio of the droplet and changes in surface tension as a result of changes in solute concentration and related surface composition. In most scenarios, only the diameter change is accounted for while the surface tension is assumed to remain constant, usually with the value for pure water ($\sigma = \sigma_w \approx 72$ mN m^{-1} at 298 K). This oversimplifies the problem, especially when organic solutes are present that adsorb at the surface of the growing droplet. In experimental studies where only the critical supersaturation or critical dry diameter are measured, this assumption can lead to errors, as the complexity of the system may not allow for such simplified treatments to yield sufficiently accurate representations of a real-world problem. In such cases, one must consider how the changing size of the droplet (or, again, more specifically the solution composition) results in changes in bulk-surface partitioning and ultimately surface tension.

Recent work has shown that a rigorous account of bulk–surface partitioning leads to complex Köhler curves whose shapes are often difficult to interpret (Ruehl et al., 2016). These shapes can be more easily understood by considering a very simple example, shown in Figure 1B. Here, a series of fixed surface tension (*iso*-σ) Köhler curves with values ranging from 72 mN m^{-1} to 30 mN m^{-1} are shown, using the same 50 nm particle (of ammonium sulfate) from Figure 1A. Distinct schematic dependences of the surface tension on the droplet size, representative of the types of dependence that might be encountered in real aerosol, are imposed for the purpose of illustration, shown in the lower panel of Figure 1B. At each point along these dependences, the saturation ratio will be determined by the position on the Köhler curve corresponding to that specific surface tension. This means that instead of following a single trajectory along an *iso*-σ curve, the system is better envisioned as traversing across these curves, producing a very different final shape to the Köhler curve than would normally be expected. In the case of a linear dependence of σ on D (black curve), the Köhler curve cuts across the *iso*-σ lines until σ reaches the value of pure water. In this case, this coincides with reaching the maximum in the droplet's saturation ratio and thus reflects the activation point. In the case shown in red, activation occurs prior to the surface tension returning to the value of pure water. In the case shown in green, activation follows a pseudo two-step process, where initially a large increase in size occurs for a small increase in supersaturation, and thus the droplet may appear to be activated, while in this case true activation occurs at the point corresponding to the intersection with the Köhler curve of $\sigma = \sigma_w$. It is important to note that it is not necessarily the magnitude of the suppression of surface tension that drives unusual activation behavior, but the dependence of the surface tension on concentration, which is dictated by the droplet size and the thermodynamics of the system.

It is apparent from these examples that an evolving surface tension may introduce ~~discontinuities~~ abrupt changes in the activation ~~process~~ curve that arise due to the phase behavior of monolayer systems. The most obvious ~~discontinuity~~ change is where the surface tension returns to the value of pure water. Following this point, the system will follow the *iso*-σ curve corresponding to pure water surface tension (under continued and sufficient supersaturation conditions). Depending on the exact relationship of surface tension and droplet size, this point can mark the activation barrier of the system, as is the case in Figure 1B for the black and green curves. This also seemingly supports previous assertions, as discussed in Section 1, that surface tension does not impact activation, since it is generally argued that at the point of activation the droplet is sufficiently dilute and essentially exhibits a surface tension like pure water (Fuentes et al., 2011; Prisle et al., 2008; Sorjamaa et al., 2004). While that is the case in this example, the trajectory of the activation process is significantly altered by the surface tension history of the droplet. In other words, for the systems described by the black or green curves in Fig. 1B, the surface tension at the point of CCN activation is that of pure water, yet if one would assume the surface tension of the droplet to be constantly that of pure water at any size prior to activation, the critical supersaturation, SS_{crit}, would be significantly higher and the critical (wet) activation diameter, D_{crit}, substantially smaller (see the Köhler curve for $\sigma = \sigma_w$). Clearly, an evolving surface tension prior to activation can matter in such systems and, consequently, knowing the surface tension only at the point of activation is in a general case insufficient for determining the critical properties at activation (absent any droplet size measurement), because the position of the maximum in the Köhler curve and, thus, the droplet size at activation, will depend on the trajectory of surface tension evolution. Moreover, knowing the surface tension at the activation point only, may not allow for an accurate prediction of whether a droplet of given dry diameter will activate at a given environmental supersaturation (compare the green curve with the *iso*-σ curve of 72 mN m^{-1} in Fig. 1B, both having the same surface tension at their points of CCN activation, yet different critical supersaturations and wet diameters).~~Clearly, an evolving surface tension prior to activation can matter in such systems and knowing the surface tension only at the point of activation is insufficient to determine the critical properties at activation, as well as whether such a droplet of given dry diameter activates for a given environmental peak supersaturation~~. Similar conclusions have been drawn previously (e.g. (Prisle et al., 2008)), although the results of Ruehl et al. (Ruehl et al., 2016) were the first to verify this experimentally. ~~The second discontinuity occurs when the surface tension is at its minimum value, corresponding to a compressed monolayer film at high solute concentration and small droplet size. Again, in this region the system follows~~

~~an *iso-σ* curve before the droplet size grows to the point where the film begins to expand and the surface tension starts increasing, as encountered in typical pressure-area isotherms.~~

3 Surface Tension Evolution During Activation

A major consequence of an evolving surface tension is that the droplet size at activation is larger, and the actual critical supersaturation depends on how surface tension varies in the droplet as it grows. These effects were directly measured using a thermal gradient chamber (TGC) (Roberts and Nenes, 2010; Ruehl et al., 2016). In the 2016 work, mixed ammonium sulfate and organic aerosols were introduced into the TGC at various supersaturations (up to and including the activation supersaturation). The size of the aerosol particles was measured under these conditions, allowing a direct measurement of the stable equilibrium branch of the Köhler curve (i.e. the size up to the point of activation). It was shown that for highly soluble and surface inactive solutes such as ammonium sulfate and sucrose, the data exhibit the behavior expected when assuming an *iso*-σ Köhler curve. However, for the case when organic acids, spanning a range of water-solubilities, were coated on ammonium sulfate particles of specific dry sizes, the measurements clearly show modifications to the Köhler curve in comparison to an *iso-σ* Köhler curve, which were explained by changes in surface tension corresponding to bulk-surface partitioning as predicted by a compressed film model. Without these observations, assuming $\sigma = \sigma_w$, one could attribute the critical supersaturation to a single, apparent κ value that describes the hygroscopic effect of the mixture of solutes in the absence of any surface tension constraints (Petters and Kreidenweis, 2007). Low solubility and low hygroscopicity species should exhibit very small κ values. However, in the case of suberic acid, for example, the CCN activation data of Ruehl et al. would require a κ value of approximately 0.5 for the organic component, assuming a fixed surface tension equal to that of water. This κ value is unphysically large considering that the molar volume ratio suggests a value of ~0.13 for suberic acid when assuming full solubility, the surface tension of pure water and ideal mixing with water. A different prediction, accounting for limited solubility and assuming a constant surface tension using the value of the saturated aqueous solution, estimates its value as $\kappa \approx 0.003$ (Kuwata et al., 2013). Moreover, the apparent κ value derived from CCN activation data of pure suberic acid particles indicates a value of ~0.001 (Kuwata et al., 2013). Invoking a surface tension model here is the only way to make physical sense of these observations, allowing even low solubility and non-hygroscopic solutes to contribute significantly to the activation efficiency in mixed droplets. The modelling approaches of Ruehl and coworkers (Ruehl et al., 2016) and Ovadnevaite and coworkers (Ovadnevaite et al., 2017) use Köhler theory with either a bulk–surface partitioning model (compressed film model) or an equilibrium gas–particle partitioning and liquid–liquid phase separation (LLPS) model with variable surface tension. Both studies also employed simplified organic film models, in which the assumption is made that all organic material resides in a water-free surface film, as options for comparison with the more sophisticated approaches.

A bulk–surface partitioning model is comprised of two components: a two-dimensional equation of state that relates the surface tension to the surface concentration, and a corresponding isotherm that relates the surface and bulk solution concentrations. In the work of Ruehl et al., the compressed film (Jura and Harkins, 1946) and Szyszkowski-Langmuir equations of states were compared. The latter has been used in several studies exploring bulk-surface partitioning in organic aerosol (Prisle et al., 2010; Sorjamaa et al., 2004; Topping et al., 2007). The compressed film model reproduced the experimental observations, capturing the complex shapes of the measured Köhler curves. The Szyszkowski-Langmuir method was unable to explain several of the observations, attributed partly to the lack of a two-dimensional phase transition between a film state and a non-film state, which is a unique feature of the compressed film model. Earlier work by Ruehl and coworkers successfully used a van der Waals equation of state to model the behavior of organic and inorganic mixed droplets at high relative humidity (Ruehl and Wilson, 2014), demonstrating the effect of surface tension following the onset of film formation once sufficient organic material was present. While we know the factors that contribute to the equation of state and isotherm for well controlled systems the enormous complexity of atmospheric aerosol presents a significant challenge in developing and utilizing a predictive general model or theoretical framework.

The equilibrium gas–particle partitioning and liquid–liquid phase separation model is based on the Aerosol Inorganic-Organic Mixtures Functional groups Activity Coefficients (AIOMFAC) model (Zuend et al., 2008; 2011), coupled to a relatively simple, phase composition- and morphology-specific surface tension model~~ (as discussed later)~~. A detailed description of this AIOMFAC-based model, its variants and sensitivities to model parameters and assumptions is given in the supplementary information of Ovadnevaite et al (2017). Briefly, the equilibrium gas–particle and liquid–liquid partitioning model is used to predict the phases and their compositions for a bulk mixture "particle", here of known dry composition, at given RH and temperature. For other applications with given total gas + particle input concentrations, the equilibrium condensed-phase concentrations can be computed as a function of RH (accounting for partitioning of semivolatiles). Assuming spherical particles of a certain dry diameter with a core-shell morphology of liquid phases in the case of LLPS, density information from all constituents is used to compute volume contributions and the size of the particle at elevated RH. In addition, the surface tension of each individual liquid phase is computed as a volume-fraction-weighted mean of the pure-component surface tension values. In the case of LLPS, the surface coverage of the (organic-rich) shell phase is evaluated by considering that it must be greater than or equal to a minimum film thickness (monolayer as a lower limit); this determines whether complete or partial surface coverage applies for a certain wet diameter. The effective surface tension of the whole particle is then computed as the surface-area-weighted mean of the surface tensions of contributing phases. This way the surface tension evolves in a physically reasonable manner as a droplet grows, including the possibility for abrupt transitions from a low surface tension, established due to full organic droplet coverage under LLPS, to partial organic film coverage after monolayer film break-up, and further to complete dissolution of organics in the aqueous inorganic-rich phase (single aqueous phase). This equilibrium model is here referred to as AIOMFAC-EQUIL. We also employed two AIOMFAC-CLLPS model variants, in which the organic constituents are assumed to reside constantly in a separate phase from ammonium sulfate (complete LLPS, an organic film), either with or without water present in that phase, discussed in Section 4. ~~This~~ This approach, introduced~~, used~~ by Ovadnevaite and coworkers (Ovadnevaite et al., 2017), shows promise due to its ability to predict the existence of a surface tension activation effect consistent with CCN observations taken in marine air containing a nascent ultrafine aerosol size mode. In that study, enhanced CCN activity of ultrafine particles was observed for aerosols consisting of organic material mixed with inorganic salts and acids in North Atlantic marine air masses, which could not be explained when accounting for hygroscopicity or solubility alone (when assuming surface tension of water). While the LLPS-based model and the compressed film model of Ruehl et al. employ different principles and descriptions to account for the surface composition, both agree that gradual surface tension changes dominate the CCN activation process for these systems. Interestingly, while the observations of Ruehl et al. showed activation occurring when the surface tension returns to its maximum value (i.e. that of pure water), the phase separation model predicted activation prior to the surface tension returning to its maximum (for ultrafine particles). As discussed by Ovadnevaite et al. (2017), this difference in the surface tension value reached at the point of CCN activation depends in some cases on the size range of the (dry) particles considered (for the same dry composition). Ovadnevaite et al. show that for particles of larger dry diameters (e.g. 175 nm for the case of their aerosol model system), CCN activation is predicted to occur at a point where the particle's surface tension has reached the value of pure water (see the Supplementary Information of that study). Hence, both observations are consistent with the picture developed in Figure 1B and the details depend on the particle size range and functional form describing the change in surface tension of the system considered. Moreover, it is important to recognize that – regardless of whether the surface tension is equivalent to or lower than that of pure water at the CCN activation point – a CCN exhibiting an evolving, lowered surface tension while approaching the activation point during hygroscopic growth will activate at a lower supersaturation than a CCN of constant surface tension equivalent to the pure-water value, since the former activates at a larger diameter, as is evident from the examples of the red and green Kohler curves shown in Fig. 1B. This predicted size effect indicates that it is not generally valid to assume that all activating CCN will have a surface tension equivalent to or close to that of pure water – nor is it appropriate to use a single measurement of the surface tension of a multicomponent CCN of known dry composition at its activation size (only) to determine its Köhler curve, as also noted in previous studies (Prisle et al., 2010; 2008; Sorjamaa et al., 2004).

Furthermore, these model predictions also suggest that measurements of the surface tension of larger CCN particles (e.g. > 150 nm dry diameter) may not allow for conclusions about the surface tension of much smaller CCN, e.g. of 50 nm dry diameter.

4 Identifying Surface Tension Effects from Critical Supersaturation

Although the LLPS-based and compressed film model of CCN activation have had some success in capturing surface tension effects, there remain substantial challenges in developing a generalized theory. One challenge is that CCN techniques do not measure surface tension directly but instead observe the effects of changes in surface tension, which may often be attributed to other factors. In order to identify surface tension effects using these techniques, experiments must be performed to maximize the scope of surface tension effects while minimizing changes in other variables that might influence observations. Here, we propose new experiments, using a model system as an example, which allows surface tension effects to be identified in the absence of other complicating factors.

Using a Cloud Condensation Nucleus Counter (CCNC, Droplet Measurement Technology), we measured the supersaturation required to activate mixed suberic acid and ammonium sulfate particles. Suberic acid was chosen to represent low solubility oxygenated organic material typical of atmospheric secondary organic aerosol. It is not a traditional surfactant, but its role in suppressing surface tension and modifying the shape of the Kohler curve has been previously identified (Ruehl et al., 2016). Ammonium sulfate particles were generated using an atomizer and dried using silica gel and a Nafion drier with dry N_2 counter flow. The size distribution was measured and a size-selected seed was introduced into a flow tube containing suberic acid and housed within a furnace oven. The temperature was set to volatilize the organic material and allow it to condense onto the seed particles up to a desired thickness. The coated particles were size-selected again and introduced into a particle counter and a Cloud Condensation Nucleus Counter (CCNC; Droplet Measurement Technologies) at a concentration of around 2000 cm^{-3}. The activated fraction was measured as a function of saturation ratio and the critical supersaturation was determined from the half-rise times of a sigmoid fit to the data. A range of dry particle sizes and organic volume fractions (f_{org}) were selected for measurements under humidified conditions at room temperature (~ 20 ºC). Notably, the coated particle (i.e. total size) of the aerosol in its dry state was kept constant across a dataset spanning a range of organic volume fractions. The CCNC was calibrated with ammonium sulfate particles at room temperature at regular intervals, although typically the calibration remained stable during continued usage.

The organic volume fraction (f_{org}) was varied while maintaining fixed dry particle sizes (Prisle et al., 2010; Wittbom et al., 2018), ensuring that any surface tension effect would not be masked by changes in the overall size, in contrast to other studies that allow both coated particle size and organic volume fraction to vary simultaneously (eg. (Hings et al., 2008; Nguyen et al., 2017)). Figure 2A shows the critical supersaturation as a function of f_{org} for 100 nm (dry diameter) mixed ammonium sulfate and suberic acid particles. Remarkably, despite the much lower hygroscopicity of suberic acid relative to ammonium sulfate, there is very little increase in the required supersaturation as the organic volume fraction increases (while the ammonium sulfate volume fraction is reduced accordingly). In fact, considering a fixed surface tension of pure water, a κ_{org} value of 0.35 for the organic fraction is required to explain these data (using $\kappa = 0.62$ for ammonium sulfate). This κ_{org} value is lower than that reported by Ruehl et al. (where $\kappa_{org} = 0.5$), although those measurements were performed on 150 nm particles at $f_{\mathrm{org}} = 0.963$. If we apply the compressed film model (using the parameters established in (Ruehl et al., 2016) for 150 nm particles at $f_{\mathrm{org}} = 0.963$) to predict the critical supersaturation as a function of f_{org}, we obtain a dependence that shows a peak SS_{crit} at $f_{\mathrm{org}} = 0.4$ (Figure 2), followed by a decrease towards higher f_{org}. This shape is consistent with the lower value of SS_{crit} reported by Ruehl et al. at $f_{\mathrm{org}} = 0.963$. ~~Although it does not reproduce the data exactly, it does more closely predict the observations across the full range of composition.~~ If we use the ideal molar volume derived κ_{org} value of 0.131 and a constant surface tension of $\sigma = \sigma_w$, the bulk solubility prediction significantly overestimates SS_{crit} for $f_{\mathrm{org}} > 0.5$. It must be noted here that without prior knowledge that suberic acid is inherently of very low hygroscopicity and exhibits low water-solubility, the prediction using $\kappa_{\mathrm{org}} = 0.35$ could be mistaken as the correct answer. However, a κ_{org} value of this magnitude is unphysical when considering the original definition of κ. One could ignore the physical meaning of κ and simply use it as an all-encompassing parameter to describe activation efficiency. In this case, the generality of the parameter to interpret observations in different conditions is lost. The compressed film model decouples the water activity component from the surface tension component, and thus should better represent the physical processes at work. However, the agreement for all these models breaks down further when looking at different sized particles. For example, Figure 2B shows the same system of ammonium sulfate and suberic acid, this time using 40 nm dry diameter particles. In this case, the required supersaturation decreases with increasing organic fraction, suggesting that suberic acid is more hygroscopic than ammonium sulfate (requiring $\kappa_{\mathrm{org}} = 0.72$). For the ultrafine aerosol size reported here, the compressed film model does a worse job at predicting the behavior, suggesting that it too suffers from a lack of generality in its applicability. What is clear, however, is that a specific suberic acid hygroscopicity alone cannot explain the observations across a range of particle sizes and compositions.

These observations are obscured when the data is reported with a fixed inorganic seed size with an increasing organic fraction achieved through an increase in the coated diameter. The data as a function of f_{org} with a fixed total diameter was used to plot SS_{crit} as a function of f_{org} with a fixed inorganic seed size, shown in Figure 2C with an arbitrarily chosen inorganic seed size of 33 nm dry diameter. The value of SS_{crit} for coated diameters 40, 50 and 100 nm was found by linear interpolation of the data in Figures 2A and 2B (and the 50 nm case in Figure 3). The data is compared against a bulk κ-Köhler prediction, which exhibits a similar trend, although with a slightly smaller slope when $\kappa_{\mathrm{org}} = 0.15$. These data are brought to agreement using $\kappa_{\mathrm{org}} = 0.4$. However, we have already shown that for the 40 nm case, a value of κ_{org} greater than that of AS is required to explain the data as a function of f_{org} with a fixed dry diameter. Specifically, in Fig. 2C, the organic volume fractions are distinctly different for the three points shown: $f_{org} = 0.40$, 0.70, and 0.96 for the 40, 50, and 100 nm coated diameter cases, respectively. Thus, ~~there is a clear loss of information simply due to~~ the choice of experimental procedure or data presentation can impact the interpretation of experimental observations and we caution care when presenting such data.~~.~~ When composition and particle size are coupled in D_{coated}, the sensitivity to surface tension effects is diminished, as smaller particles will contain a lower volume fraction of organic material.

For both sets of measurements, we also applied three model predictions based on the Aerosol Inorganic-Organic Mixtures Functional groups Activity Coefficients (AIOMFAC) (Zuend et al., 2008; 2011) model with LLPS and a phase-specific surface tension mixing rule considered. The full equilibrium calculation, labeled as AIOMFAC-EQUIL in Figure 2, considers the potential existence of a bulk liquid–liquid equilibrium, resulting in two liquid phases of distinct compositions yet each containing some amounts of all three components. The chemical compositions affect the surface tensions of the individual phases and, using a core-shell morphology assumption and minimum phase (film) thickness, that of the overall droplet. For the calculations performed, suberic acid is assumed to be in a liquid state at high water activity. This model predicts an LLPS for the aqueous suberic acid + ammonium sulfate system, but only up to a certain water activity level < 0.99, beyond which a single liquid phase is the stable state. The upper limit of LLPS predicted increases with the fraction of suberic acid in the system: LLPS onset $a_w \approx 0.942$ for $f_{org} = 0.27$ to $a_w \approx 0.983$ for $f_{org} = 0.88$. This results in the absence of LLPS at supersaturated conditions prior to CCN activation for both dry particle diameters considered. Therefore, the AIOMFAC-EQUIL prediction does not lead to a significant surface tension reduction here, which explains why the predicted SS_{crit} in Fig. 2 is similar to that of an iso-σ κ-Köhler model with $\kappa_{org} \approx 0.13$. The two AIOMFAC-CLLPS variants represent simplified model calculations in which the assumption is made that dissolved aqueous electrolytes and organics always reside in separate phases regardless of water content. In the variant labeled AIOMFAC-CLLPS (w/ org film), all organic material is assumed to reside in a water-free organic shell-phase (an organic film) at the surface of the aqueous droplet. This assumption leads to a maximum possible surface tension lowering up to relatively large droplet sizes (for intermediate to high f_{org}), yet a reduced solute effect, especially for high f_{org}. The variant labelled AIOMFAC-CLLPS (w/o org film) in Fig. 2 differs by allowing water to partition to the organic-rich shell phase (in equilibrium with the target water activity), which may affect the surface tension of that phase. Due to a significant water uptake by suberic acid, predicted to occur for $a_w > 0.99$, the resulting surface tension prior to and near activation is that of pure water and the SS_{crit} prediction resembles that of the AIOMFAC-EQUIL case. Physical parameters used in these simulations are presented in Table 1 and a schematic representation of these cases is shown in Figure A1. A comparison of predicted Köhler curves from these model variants is shown in Fig. A2 for the case of $f_{org} = 0.58$. The AIOMFAC-based predictions of critical dry diameters and SS_{crit} are listed in Table 2 for a range of dry diameters. A comparison of the different models with experimental data in Fig. 2 indicate that for $f_{org} > 0.3$, the simplified organic film model variant AIOMFAC-CLLPS (w/ org film) offers the best agreement with the measurements. This observation is consistent with the results of (Prisle et al., 2011) who applied a similar simple model to droplets containing ionic surfactants and ~~This~~ hints at a significant suppression of surface tension by suberic acid, which is likely highly enriched at the droplet surface.

~~However~~Unfortunately, neither of the models fully captures the observed behavior at all f_{org} and size regimes, and is suggestive that additional factors that have yet to be fully identified may influence the activation process. As discussed by Ovadnevaite and coworkers (Ovadnevaite et al., 2017), the AIOMFAC-EQUIL and AIOMFAC-CLLPS (w/ org film) calculations may provide upper and lower bounds on the prediction of SS_{crit} for a given system, which is roughly in agreement with the data in Fig. 2. In reality, it is likely that some portion of suberic acid dissolves into the aqueous droplet bulk at high relative humidity, itself contributing to the water uptake of the droplet, as predicted by AIOMFAC-EQUIL, while a significant organic enrichment prevails at the surface, lowering the surface tension and consequently SS_{crit}. Such behavior could explain the data and the increasing model-measurement deviations towards higher f_{org}. Improvements of the AIOMFAC-based models with more sophisticated bulk–surface partitioning treatments in individual liquid phases seem to offer a way forward to address some of the observed shortcomings in future work. At this point, it remains intriguing that the simplified organic film model provides the best description of these experimental data, even though its restrictive assumptions about phase separation and organic water content seem to make it a less physically realistic model variant.

These types of experiment also expose further factors that influence CCN activation, possibly through modification to surface partitioning, such as the role of inorganic ions. We performed additional measurements using different inorganic seed particles coated with suberic acid and observed vastly different behavior across three different salts (ammonium sulfate, sodium iodide and sodium carbonate), shown in Figure 3 for 50 nm dry diameter particles. We see for ammonium sulfate the same qualitative behavior as for the other two sizes already discussed; in contrast, the responses of the systems containing the other salts (all with suberic acid as the organic component) are very different. Sodium carbonate exhibits an increase in the required critical supersaturation across the range of compositions; a trend that could reasonably be predicted without invoking surface tension effects. The trend with sodium iodide is more complex and appears to show a sharp discontinuity near $f_{\mathrm{org}} = 0.5$, which was highly reproducible across multiple repeat experiments over multiple days. These salts were chosen to span the range of the Hofmeister series, which describes the propensity of inorganic ions to salt in or salt out organic molecules (proteins in particular). Sulfate and carbonate are the best salting-out ions, while iodide has a relatively weak salting-out effect due to its own surface propensity (Santos et al., 2010). It is interesting to note the differences between carbonate and sulfate, despite their similar position on the Hofmeister scale. The role of the cation is generally considered to be much smaller than that of the anion, thus these differences are non-trivial. These results serve to further highlight a key conclusion of this work – that we currently lack a robust molecular model that is capable of describing and therefore accurately predicting CCN hygroscopicity and activation even in a relatively simple model system. We hope to prompt further discussions and experimental studies to explore these observations and bulk/surface composition effects on surface tension and CCN activation in more detail.

5 Summary and Conclusions

Surface tension effects can lead to significant differences from classic, hygroscopicity mixing rule mechanisms for CCN activation (Hansen et al., 2015; Kristensen et al., 2014). While it has already been made clear that the activation diameter can be significantly different from that determined by an *iso-σ*

Köhler curve, in this work we reveal the potential for more subtle changes in CCN activity (both increases and decreases relative to pure ammonium sulfate particles) as a result of the organics-influenced surface tension evolution during droplet growth. These changes were captured by measuring particles at a fixed diameter with a range of organic volume fractions. Ultimately, to derive an accurate picture of CCN activity across the relevant ranges of chemical compositions and size distributions, the effects of surface tension variability must be taken into account. It should be noted, however, that there are many situations where using simple mixing rules with inferred values for κ_{org} can lead to sufficiently accurate predictions without the need for more complex analyses or simulations. It is therefore of key importance to constrain the conditions under which simple approaches are justified – and to know when they may be inappropriate. Taking the activation model based on Köhler theory forward will require a more rigorous interrogation of the role of co-solutes in partitioning, and ultimately an assessment of its effect in real-world simulations of cloud formation.

In the meantime, it is important for environmental scientists to recognize the conditions in which surface effects may be influencing cloud droplet formation, e.g., low solubility or insoluble organics mixed with inorganic salts, high-RH phase separation, small particle sizes with critical supersaturations close to the peak supersaturations experienced in clouds, etc. We suggest, if possible, that experimental data be explored as a function of organic volume fraction while keeping the overall dry particle size the same, as from our laboratory experiments this dependence shows the most clear indicator of an unexplained size effect that may be attributed to bulk–surface partitioning. In experiments where both size and composition vary, the contribution from each is less clear and the effect of the organic component due to bulk–surface partitioning could be hidden. Further fundamental laboratory and modeling studies being performed will allow for in-depth testing and refinements of the proposed models and mechanisms that describe bulk–surface partitioning and surface tension, ultimately reaching towards a robust and universal mechanism that allows both hygroscopicity and surface tension effects to be coupled into a practical framework.

Acknowledgements

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Table 1: Value of physical parameters used in AIOMFAC calculations. Density of mixtures were calculated as a linear (additive) combination of the apparent molar volumes of the contributions of water, ammonium sulfate (AS), and suberic acid.

Calculation parameter	Value	Unit
Temperature, T	293.15	K
Pure comp. surface tension water (at T) (Vargaftik et al., 1983)	72.75	mJ m^{-2}
Pure comp. surface tension Suberic Acid (at T) *	35.00	mJ m^{-2}
~~Pure comp. surface tension~~Surface tension of aqueous AS (at T) **	72.75	mJ m^{-2}
Density of pure water (liq.) at T	997	kg m^{-3}
Density of pure suberic acid (liq.) at T	1220	kg m^{-3}
Density of pure AS (liq.) at T (Clegg and Wexler, 2011)	1550	kg m^{-3}
Density of pure AS (solid) at T (Clegg and Wexler, 2011)	1770	kg m^{-3}
Minimum shell phase thickness, $\delta_{\beta,\min}$	0.3	nm

*Value taken from measurements for of adipic acid (Riipinen et al., 2007) on the basis of structural similarity to suberic acid. **Assumption of no influence on droplet surface tension compared to water here (since highly dilute).

Table 2: Critical supersaturation SS_{crit} (%) for given dry diameters ($D_{dry,crit}$) and organic volume fractions (f_{org}) in dry particle at T = 293.15 K; predicted by the different AIOMFAC-based models.

AIOMFAC-EQUIL; with liquid–liquid phase separation considered when predicted

Mixture		Dry diameter [nm] (of overall particle)											
Solutes	f_{org}	30	35	40	45	50	60	80	100	120	140	160	200
AS	0.00	1.005	0.788	0.639	0.532	0.451	0.339	0.217	0.154	0.116	0.091	0.074	0.053
Suberic + AS	0.27	1.135	0.893	0.726	0.605	0.513	0.387	0.248	0.176	0.133	0.105	0.085	0.061
Suberic + AS	0.40	1.214	0.957	0.779	0.649	0.552	0.416	0.267	0.190	0.143	0.113	0.092	0.066
Suberic + AS	0.58	1.350	1.068	0.871	0.727	0.619	0.468	0.301	0.214	0.162	0.128	0.105	0.074
Suberic + AS	0.75	1.532	1.214	0.993	0.831	0.708	0.537	0.347	0.247	0.187	0.148	0.121	0.086
Suberic + AS	0.88	1.751	1.389	1.136	0.951	0.811	0.616	0.399	0.285	0.216	0.172	0.140	0.100

AIOMFAC-CLLPS (w/ org film); organic phase assumed water-free

Solutes	f_{org}	30	35	40	45	50	60	80	100	120	140	160	200
Suberic + AS	0.27	0.972	0.766	0.624	0.520	0.442	0.334	0.215	0.153	0.116	0.091	0.075	0.053
Suberic + AS	0.40	0.961	0.759	0.618	0.516	0.439	0.333	0.214	0.153	0.116	0.092	0.075	0.053
Suberic + AS	0.58	0.950	0.751	0.613	0.513	0.437	0.331	0.214	0.153	0.116	0.092	0.075	0.054
Suberic + AS	0.75	0.944	0.747	0.611	0.511	0.436	0.331	0.214	0.153	0.116	0.092	0.076	0.054
Suberic + AS	0.88	0.987	0.781	0.637	0.532	0.453	0.342	0.220	0.156	0.118	0.093	0.076	0.054

AIOMFAC-CLLPS (w/o org film); water uptake by organic-rich phase considered

Solutes	f_{org}	30	35	40	45	50	60	80	100	120	140	160	200
Suberic + AS	0.27	1.108	0.878	0.716	0.598	0.509	0.385	0.247	0.176	0.133	0.105	0.085	0.061
Suberic + AS	0.40	1.197	0.948	0.774	0.646	0.550	0.416	0.267	0.190	0.144	0.113	0.092	0.066
Suberic + AS	0.58	1.357	1.075	0.877	0.733	0.624	0.472	0.303	0.216	0.163	0.129	0.105	0.075
Suberic + AS	0.75	1.579	1.246	1.017	0.849	0.723	0.547	0.352	0.250	0.189	0.150	0.122	0.087
Suberic + AS	0.88	1.999	1.592	1.303	1.089	0.926	0.697	0.443	0.301	0.220	0.174	0.142	0.101

Table 3: Experimentally measured critical supersaturation for given dry diameter, inorganic particle core, and organic volume fraction.

D_{dry} / nm	Inorganic	f_{org}	SS_{crit} (%)
100	$(NH_4)_2SO_4$	0.00	0.16
		0.27	0.17
		0.58	0.17
		0.88	0.19
40	$(NH_4)_2SO_4$	0.00	0.66
		0.33	0.62
		0.58	0.57
		0.88	0.60
50	$(NH_4)_2SO_4$	0.00	0.45
		0.27	0.45
		0.41	0.42
		0.66	0.41
		0.88	0.39
50	NaI	0.00	0.38
		0.27	0.41
		0.41	0.43
		0.49	0.45
		0.53	0.41
		0.56	0.41
		0.66	0.42
		0.78	0.45
		0.88	0.48
50	Na_2CO_3	0.00	0.33
		0.27	0.34
		0.49	0.35
		0.66	0.41
		0.78	0.42
		0.88	0.44

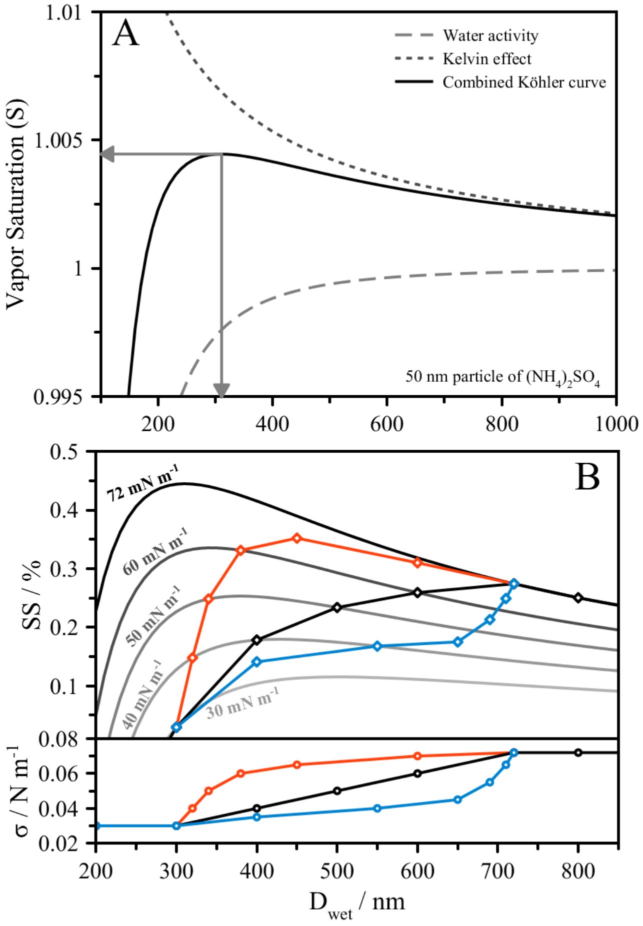

Figure 1: (A) Köhler curve construction from the combination of the water activity term and the Kelvin effect, shown here for 50 nm particles of ammonium sulfate. The arrows indicate the critical supersaturation (SS_{crit}) and the critical wet activation diameter (D_{crit}). (B) Köhler curves (NB. $SS = (S-1) \times 100\ \%$) of varying fixed surface tension values for 50 nm (dry diameter) particles with water activity treated as an ammonium sulfate solution. A schematic linear dependence of surface tension on droplet diameter is shown in black, and the Köhler curve construction that takes into account the change in surface tension is shown in bold and with diamond symbols. Additional surface tension dependencies are shown in red, which exhibits activation at $\sigma < \sigma_w$, and in ~~green~~blue, which shows a dramatic increase in the critical wet diameter.

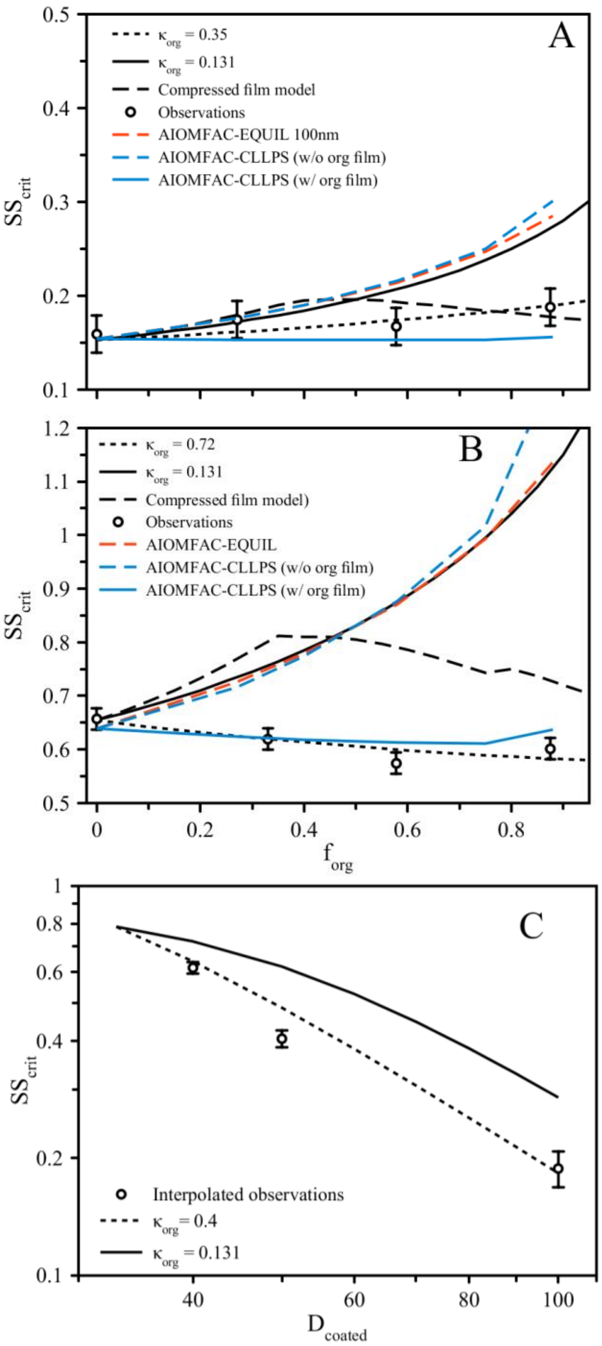

Figure 2: (A) Measured critical supersaturation (SS_{crit}) of size-selected ammonium sulfate particles coated with suberic acid (points) to a set dry diameter of 100 nm at $T \approx 293$ K. The curves show predictions from the compressed film model of Ruehl et al., a simple κ-Köhler model with constant surface tension, and model variants from the AIOMFAC-based framework (see text). (B) Analogous to (A) but for particles of ammonium sulfate coated to 40 nm dry diameter by suberic acid. (C) Using the data from panels A and B, SS_{crit} is shown as a function of coated diameter with a fixed inorganic seed of 33 nm (points). The lines indicate the κ-Köhler model with constant surface tension using different but constant values of κ_{org}.

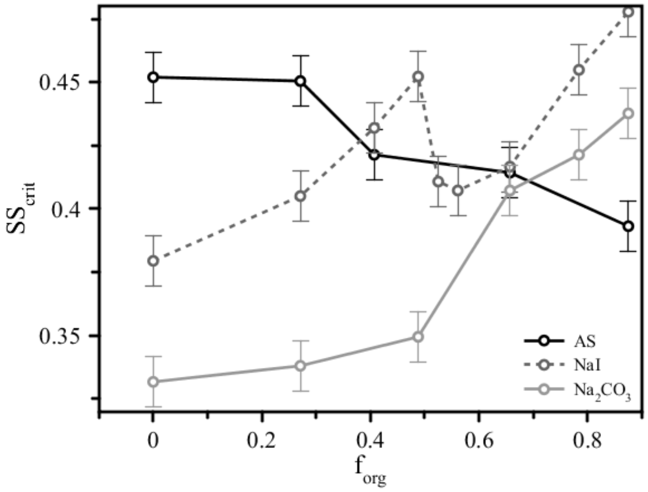

Figure 3: The measured critical supersaturation for 50 nm dry diameter particles comprised of different salts (ammonium sulfate, sodium iodide and sodium carbonate) and variable volume fractions of suberic acid (f_{org}) at $T \approx 293$ K.

Appendix

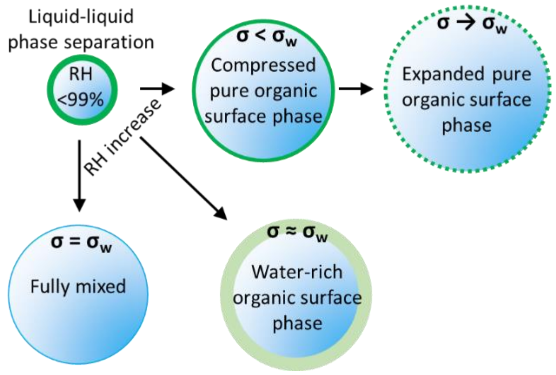

Figure A1: Schematic representation of the three model variants. AIOMFAC-EQUIL treats the droplets as a fully mixed single phase, with the surface tension of the wet droplet sharply approaching σ_w. The phase separated variants considered a surface phase that is water-rich, with surface tension close to σ_w, and a surface phase that excludes water, behaving as an organic surface film, with $\sigma < \sigma_w$. The output from these scenarios are shown in Figure A2.

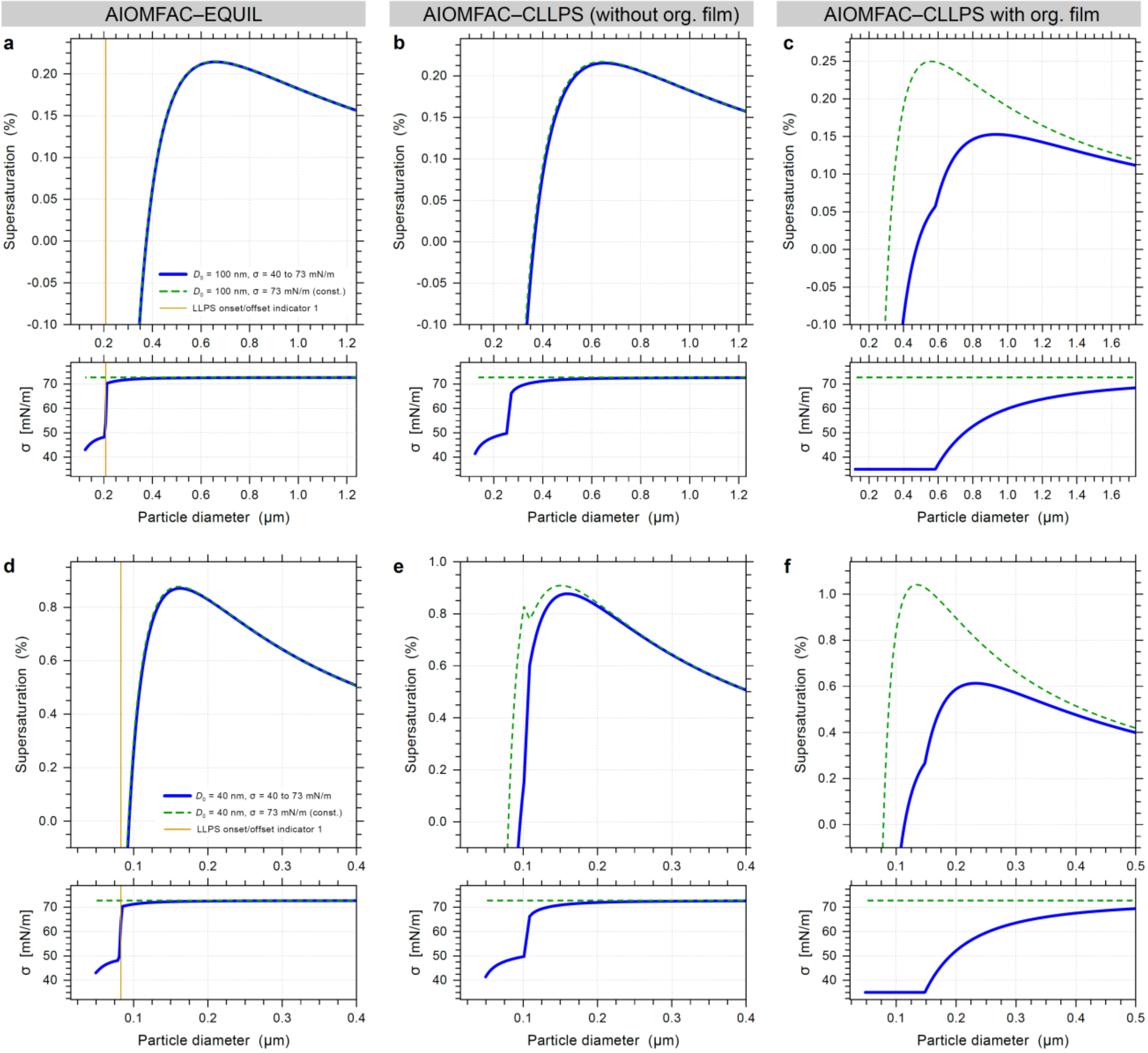

Figure A2: Predicted Köhler curves and associated droplet surface tensions for 100 nm (a, b, c) and 40 nm (d, e, f) dry diameter particles of ammonium sulfate with suberic acid at f_{org} = *0.58* using the AIOMFAC models described in the main text. The AIOMFAC-CLLPS with org. film gives the closest predictions to the experimental observations and predicts similar shaped curves to those measured experimentally by (Ruehl et al., 2016).

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