Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2019-172-AC1, 2019

Atmospheric Chemistry and Physics Discussions
Open Access

Interactive comment on "Influence of the dry aerosol particle size distribution and morphology on the cloud condensation nuclei activation. An experimental and theoretical investigation" *by* Junteng Wu et al.

Junteng Wu et al.

alessandro.faccinetto@univ-lille.fr

Received and published: 13 August 2019

Object – Answers to the Reviewers for the paper: "Influence of the dry aerosol particle size distribution and morphology on the cloud condensation nuclei activation. An experimental and theoretical investigation", Ref. ACP-2019-172.

Dear Editor, dear Reviewers, We would like to thank the Editorial Board for considering our paper ÂńInfluence of the dry aerosol particle size distribution and morphology on the cloud condensation nuclei activation. An experimental and theoretical inves-

Printer-friendly version

Discussion paper

tigationÂż for publication in ACP. We would also like to thank the Reviewers for the extensive amount of work that they clearly dedicated to our paper, we greatly appreciated their constructive comments and suggestions. We have carefully studied the comments, and the original paper has been thoroughly revised accordingly (please see here attached the revised paper, all modifications are highlighted in blue font color). In particular, as suggested by the Reviewers, the paper goal has been re-framed to focus on the effect of the particle morphology on activation and on the different response to chemical aging of soot having different properties. The data treatment has been updated to account for the multiple charges effect, the DMA transfer function has been used, a probability distribution of the parameter kappa has been introduced and one of the test distributions obtained with ammonium sulfate has been replaced with original results obtained on soot at 70 mm HAB. A detailed point by point rebuttal can be found at the end of this document. With our best regards,

Dr. Alessandro Faccinetto on behalf of all Authors.

Answers to anonymous Referee #1.

Overview. Wu et al. present laboratory data and theoretical modeling to treat the influence of particle morphology on CCN activation spectra. Size distribution data and the k-Kohler parameterization are combined to predict the CCN number concentration as a function of supersaturation. Fractal dimension inferred from single particle transmission electron microscopy experiments is folded into the analysis. The method is tested using ammonium sulfate and soot particles from a miniCAST burner. K-values for soot as a function of ozone exposure are presented. This manuscript is not suitable for publication in ACP, according to the journal standard to publish studies “with general implications for atmospheric science“. The paper does not reach clear new conclusions, mostly focuses on methodology and would be more suitable for AMT. More importantly, the manuscript lacks context of a large body of published literature, needs additional analysis folding in DMA transfer function models, and will require significant rewriting to become acceptable for publication.

Major comments. (1) Eqs. (11) and (12), “the master equations” of the work are simply a cumulative size or supersaturation distributions that have been used in similar for decades in droplet activation schemes or closure studies (e.g. Abdul-Razzak and Gahn, 2000, Snider et al., 2003 and references therein).

Answer. We did our best to cover the most significant works in the field, and we thank the Reviewer for providing some examples of literature that we did not cited or that we missed. It is indeed true that the droplet activation of aerosol particles has been parameterized in the past by using a cumulative function of the lognormal distribution (Abdul-Razzak et al. 1998). The cumulative function has been used as well for predicting the type of the aerosol measured in the outdoor measurements (Snider et al. 2003). However, we would like to notice that especially in recent literature or in works more strictly related to combustion (our field) that investigate the activation of soot particles (Sullivan et al. 2009, Lambe et al. 2015; Tang et al. 2015), sigmoid function are still used for the determination of the critical supersaturation. Therefore, we believed this topic worthy to be discussed. Please notice that in response to this and to comments (2), (3), (4) and (6) the Introduction, Theory and Results and Discussion sections have been heavily updated or entirely rewritten: the more “tutorial-like” parts are reduced to the minimum required for presenting the research context (Eq. 2 in the Introduction and section 2.1), all the missing references are added and the paper is re-framed to focus on the effect of the morphology on soot activation.

(2) In general, the work herein can be interpreted either as a laboratory CCN closure experiment or an improvement to constrain laboratory inferred k-values from data. No studies in that context are cited. For example, it has long been recognized that k-values derived from CCN data are “effective” or “apparent” k-values that have folded in effects of surface tension, solubility, and particle morphology (e.g. Poschl et al., 2009, Sullivan et al., 2010). CCN closure experiments that take size distribution data, composition and shape have been performed extensively on ambient aerosol. Studies that account for particle shape in the calibration of CCN instruments using DMAs and non-spherical

particles are routine (e.g. Snider et al., 2006, Rose et al., 2008, Kuwata and Kondo, 2009). Using TEM to obtain particle shape may be novel here (this referee is not 100% sure), but the concepts described in Section 2 are well established.

Answer. In the original formulation of kappa-Köhler theory (Petters and Kreidenweis 2007), kappa is used to estimate the chemical activity of water in a multicomponent system. Indeed, an effective/apparent kappa has been defined and often used to account for surface tension, solubility and particle morphology effects as mentioned by the Reviewer. Furthermore, a shape factor has been considered to correct the difference between the experimental activation and simulated activation of irregular inorganic aerosol particles (Rose et al. 2008, Snider et al. 2006, Biskos et al. 2006). A similar approach has been used as well on the activation study of soot particles (Lambe et al. 2015), and in particular a volume equivalent diameter has been introduced to avoid the crossing of the Kelvin limit (Tritscher et al. 2011, Lambe et al. 2015). Please also see comment (16) for more details. Following this last approach, in our work we aim to provide a method for the estimation of the volume equivalent diameter dve of soot particles that accounts for the aggregate size and morphology rather than relegating all the deviations from the expected activation curves to the effective/apparent kappa. In our opinion, “de coupling” the effective/apparent kappa and integrating size and morphology effects in dve has the potential advantage of preserving kappa as an indicator of the chemistry at the particle surface for instance. Please notice that in response to this comment, the old section 2 has been completely replaced with the derivation of the morphology-corrected dve.

(3) The “master equation” (Eq. 11) cannot be applied to DMA distributions. The role of the DMA transfer function and of multiply charged particles needs to be taken into account (e.g. Petters, 2018). It is clear that the effect of multiply charge particles is not large as shown by the shoulder in Figure 6. However, the paper makes claims about kappa being a “Dirac delta distribution”, i.e. a single value applied to a distribution. The question is whether the observed activation behavior is due to size distribution alone,

or whether shape and composition heterogeneity increases the broadness. Therefore, Eq. (11) should be replaced with the DMA transfer function, including multiply charged particles, and the use unexplained discrepancies to identify the effect of shape and/or heterogeneity. (4) The influences of size distribution heterogeneity and particle shape on the cumulative CCN spectrum have been discussed in the literature (e.g. Petters et al., 2009, Kuwata and Kondo, 2009, Su et al., 2010, Cerully et al., 2011). The work of Su et al. is particularly pertinent to this paper.

Answer. Being comments (3) and (4) strictly related, one comprehensive answer is provided. We acknowledge that this could have been better explained in our original manuscript, and we thank the Reviewer for providing the pertinent literature references. Indeed, in our original work we used a single value instead of a distribution to describe kappa, and we observed that the geometrical standard deviation (σg = 1.08) of soot distribution recorded by SMPS is smaller than the value (σg = 1.16) in Eq. (22) obtained by fitting experimental activation curves. This discrepancy was acknowledged but not explained. In response to these comments, in the revised version of the paper all calculations have been updated to take into account the DMA transfer function and the effect of multiply charged particles (the effect on the ammonium sulfate is important and cannot be neglected, however the effect on soot is comparatively small). Furthermore, a distribution rather than a single kappa value was tested. As the Reviewer suggested, the updated σg values are now consistent, and therefore the kappa distribution (Su et al. 2010, Cerully et al. 2011) has been applied to all calculation and discussed in the revised version of the paper in the updated Theory and Results and Discussion sections.

(5) The aging studies of miniCAST soot are interesting. However, it is important to place these results in the context of several similar studies that have investigated the CCN activity of (chemically aged) soot.

Answer. We would like to emphasize that this work is not about miniCAST soot, but about the chemical aging of young and mature soot sampled from a laboratory turbulent jet flame supplied with liquid kerosene. Unlike miniCAST that provides only the soot that can be recovered in the exhausts, laboratory flames allow the generation of soot having controlled properties in terms of aggregate size distribution, morphology and surface chemical composition that are accessed by sampling the flame in the axis at different reaction time (or equivalently height above the burner, HAB). In a miniCAST burner there is no direct access to the flame, and therefore only the exhausts are routinely sampled that leads to several important limitations (contamination of the sampled soot with the exhaust gas phase, sampling of particles formed in very different conditions and mixed only at the end of the combustion process to name a few). Clarifications have been added to the Introduction, and the Results and Discussion section has been re-framed to focus on this aspect. To the best of our knowledge, the closest studies to our work are (Tritscher et al. 2011) and (Lambe et al. 2015), both referenced in the original paper, in which the approximated equation for kappa > 0.2 is used. The implications on the use of such approximation for the interpretation of the activation curves were discussed in the original paper (old Figure 9), but rendered obsolete after revision. The Results and Discussion section has been updated to match.

(6) The framing around improving k-Kohler or Kohler theory in general is not justified. Kohler theory predicts the activation behavior of a single particle. If one applies that theory recursively to a size distribution with non-uniform composition, or a shaped particle, then those assumption need to be questioned, as it has been in previous studies. Statements that “[f]or all practical purposes, both theories operate under the hypothesis of Dirac delta distributions” don’t really make sense in that context.

Answer. The particle size distribution (Snider et al. 2003) and the heterogeneity of kappa (Su et al. 2010) both influence the activation behavior and have been taken into account in the improved data treatment after revision. The hypothesis of Dirac delta distribution was initially proposed for a group of uniform size particles with constant morphology and chemical composition (for example ammonium sulfate). In our work, the comparison of σg obtained from experimental SMPS size distribution and from fitted activation spectra demonstrated that the modifications of the heterogeneity of aged soot particles is indeed a concern during the aging process. However, in the revised version of the paper, the main goals have been re defined to focus on the role of the particle morphology on activation and on the difference in the behavior of young and mature soot. More emphasis is given to original results rather than well established knowledge. For instance, one distribution on test ammonium sulfate has been replaced with a complete description of the results on soot at 70 mm HAB, and a more detailed discussion has been developed. The Introduction, Theory and Results and Discussion sections have been heavily updated or entirely rewritten. Overall, the paper has been made less pedagogic (removal of the “tutorial” section, focus from the very beginning on the morphology, removed some redundant text).

(7) It is not clear what the main finding of the work is. Equations are presented and somewhat successfully tested against experimental data, but that type of exercise has been presented before. The novelty of the work and the scientific findings contributed need to be better articulated.

Answer. All requested modifications are included in the revised version of the paper, please see answers to point (2), (5) and (6) for more details. Briefly, the main results include: “de coupling” the particle morphology from the effective/apparent kappa and integrating size and morphology effects in dve to preserving kappa as an “all-chemistry” indicator; providing evidence that chemically aged young and mature soot behave very differently during activation experiments, and thus showing that the soot generation process is critically important for this kind of experiments; providing a lower limit for the validity of the model (kappaâĹij5×10-6) by using chemically aged soot particles characterized by kappa values typically 2-3 orders of magnitude lower than typical inorganic aerosols used in activation experiments. The Results and Discussion sections have been heavily updated to focus on the main results.

(8) The writing of the manuscript needs to be improved significantly. Words are frequently used incorrectly. The writing lacks context of important prior literature. The

Printer-friendly version

Discussion paper

framing of the work needs to be revised. Section 2 reads more like a tutorial than a scientific paper.

Answer. The manuscript has been thoroughly revised, and all the corrections suggested by the Reviewers implemented and/or discussed in detail. In particular, the Introduction and Theory sections have been entirely reworked to remove the feeling of “reading a tutorial” and to include and discuss the missing suggested literature. The Discussion section has been modified as well to account for the improved data treatment as suggested. Unfortunately, none of the Authors is a native English speaker. We did our best to keep up with the quality standards of ACP, and kindly thank the Reviewers for all the given suggestions aiming to improve the English level.

(9) The data availability is inconsistent with the journal policy. The data should be deposited in a publicly available repository.

Answer. All corresponding data will be uploaded in a publicly available repository.

Other comments. (10) To my understanding Köhler theory isn’t equivalent to “classical nucleation theory”, which usually refers to homogeneous nucleation.

Answer. Corrected (this sentence has been removed in the re framing process).

(11) The second part of the sentence isn’t quite parsable. Is this talking about density profiles within a particle? Or differences in density and composition within a distribution. Given the context of the paper, it seems to be the latter. k-Köhler treats the activation of a single particle. It therefore does not make any assumptions about the heterogeneity of the size distribution.”

Answer. Corrected (this sentence has been removed in the re framing process).

(12) To the present day–please rephrase

Answer. Corrected.

(13) “internally mixed nature—internally mixed refers to a distribution property (i.e. two

substances may be internally mixed or externally mixed across a distribution). A single particle is either pure or mixed. k-Köhler theory is one means to treat the activation of mixed particles."

Answer. Corrected (this sentence aimed to highlight the mixed nature of the single particle, and it been removed in the re framing process).

(14) partially soluble—please change to sparingly soluble. The state of dissolution is determined by the water content. A substance may be "partially dissolved" but it has a strictly defined solubility value.

Answer. "Partially soluble" is a non quantitative, descriptive locution commonly used in chemistry to indicate small but unknown solubility product constants Kps.

(15) Response to comment: "neither the classical nor the k-Köhler theory account for the dry aerosol particle size distribution and morphology—this is not the objective of those theories. This is a problem on how it is applied in practice."

Answer. Corrected (this sentence has been removed in the re framing process).

(16) more specifically, the crossing of the Kelvin limit has been reported in several instances—Please explain what is meant by that.

Answer. According to the kappa-Köhler theory, a non-soluble particle (kappa = 0) could be activated to form a water droplet by increasing the supersaturation up to the so called Kelvin limit. However, soot particles are sometimes found beyond this limit if the mobility size or the volume equivalent size are used (Tritscher et al. 2011, Lambe et al. 2015). In the frame of kappa-Köhler theory, this leads to $k < 0$ that has no physical meaning. This point is now clarified in the Introduction and Results and Discussion sections of the revised paper in the context of the improved data treatment and interpretation suggested by the Reviewer in points (2), (3), (4) and (6).

(17) is the master equation of this work—this is an odd formulation

Answer. Corrected (this sentence has been removed in the re framing process).

(18) geometric deviation—geometric standard deviation

Answer. Corrected.

(19) and the fitting is implicitly assumed not to carry any physically meaningful parameter. — not true. See Cerrully et al. 2011, Figure 3.

Answer. A sigmoid curve is used in (Cerully et al. 2011). The slope of the sigmoid curve is explained by the degree of heterogeneity of activated particles. However, if the lognormal distribution of aerosol particles is used, figure 4d in the original paper clearly indicates that the activation curve is far from the sigmoid curve when σg increases. This point is now clarified in the Introduction in the context of the improved data treatment and interpretation suggested by the Reviewer in points (2), (3), (4) and (6).

(20) within 20% incertitude—within 20% uncertainty

Answer. Corrected.

(21) soot emissions are emblematic of human activities—please reword

Answer. Corrected.

(22) understanding the anthropogenic impact on the atmosphere—please reword

Answer. Corrected (this sentence has been removed in the re framing process).

(23) please specify what “very representative” means. Is there a metric for this?

Answer. The fractal dimension obtained for soot particles from 2D TEM analysis in this work spans the range 1.65-1.67 that is quite consistent with values in the range 1.61-1.82 typically found in the literature. Corrected.

(24) univocally defined—is defined

Answer. Corrected.

Printer-friendly version

Discussion paper

(25) “Young soot; mature soot—Soot aren’t biological entities. Fresh soot and chemically aged soot would appear to be better terms.”

Answer. “Young soot” and “mature soot” are well established descriptive terms used in the combustion community and related to the permanence time of soot inside the flame (or equivalently to the height above the burner, HAB). See for instance (Mitra et al. Combust. Flame 2019, Cain et al. PCCP 2014, Alfé et al. Proc. Combust. Inst. 2009). In a turbulent diffusion flame like the one investigated in this work, “young soot” refers to the condensed phase matter sampled at short reaction time (or low HAB) and characterized by high H/C ratio (typically $H/C > 0.7$) and small aggregates of 14-15 nm primary particles. On the other hand, “mature soot” refers to the matter sampled at long reaction time (or high HAB), characterized by low H/C ratio (typically < 0.4) that results in a much slower reactivity during the aging process. Furthermore, with respect to young soot, the aggregates are larger both in their number of primary particles per aggregate and in the size of the primary particles (16-17 nm). In other words, it is very well possible to have young fresh soot or young chemically aged soot, opposed to mature fresh soot or mature chemically aged soot. The different behavior of young and mature soot to chemical aging is actually one of the main points of our paper, and such investigation is mainly possible because of the precise control over the flame conditions allowed by the use of a laboratory flame rather than a commercial burner. A more accurate and detailed discussion has been added to the Introduction.

(26) k-Köhler theory is built around the idea that the soluble fraction only affects the heterogeneous nucleation—this is not strictly true. k-Köhler can be used to parameterize CCN activity descriptively, even if the underlying mechanism is incorrect. Such parameterizations have been termed “apparent k” or “effective k” in the literature.

Answer. Corrected (a specific sentence has been added to the Introduction).

(27) k parameterizes all the information on the composition of the droplet approximated as an ideal water solution—this is incorrect. K is a one parameter activity coefficient

model that explicitly models the non-ideality at the point of activation.

Answer. Corrected. Please also see answers to point (2).

(28) Incidentally, the effect of the dry particle electrical charge on the activation is not considered in this work.—This is unclear what this means. As written, it suggests that particle charge itself affects activation. To my knowledge there is no evidence for such a claim. If it is meant that the effect of particle charge on selected size is not considered, this is correct and needs to be addressed (see major comment)."

Answer. Corrected (the effect of multiply charged particles is now taken into account in the data treatment, and a specific sentence has been added to the Introduction).

Answers to anonymous Referee #2.

Overview. Wu et al. focus on the CCN activity of particles with irregular shape through a combination of theory and experimental data. Although the study contains interesting material, I feel it cannot be published in its current form and unfortunately must recommend rejection to provide the authors enough time to prepare a modified manuscript. Overall this study contains a very large amount of material that is not wrong, but is "textbook", often without reference to any of the large body of published literature on the subject. I strongly recommend that the authors give appropriate credit to the published work, but also keep only what is absolutely necessary. Reviewer #1 presents a few references, I can add also the textbooks of Seinfeld & Pandis, Pruppacher and Klett, as well as review of state-of-the art mechanistic parameterizations (e.g., from the groups of Ghan or Nenes) – which normally adopt formulations that use lognormals (e.g., Fountoukis and Nenes, 2005). There is now a rich literature based upon CCN spectral analysis to constrain hygroscopicity – considering shape factors, multiple charging and DMA transfer function effects (e.g., Cerully et al., 2011 and references therein) – even for well established calibration aerosol like sodium chloride and ammonium sulfate.

Major comments. (1) What I suggest is that the authors consider a resubmission, focusing on the results of the soot activation experiments, and also comparing them to existing literature. In their analysis it is nice that shape effects are considered, and even nicer that the fractal dimension is explicitly determined, because it allows then to explore other theories of activation such as adsorption-activation theory (e.g., Kumar et al., 2009; Laaksonen et al., 2016 and references therein) – alone or in combination with Kohler theory. It would be interesting to see how this other framework performs and if it can provide insight on the drivers of CCN activity for the particles studied.

Answer. Being comments (1) and (6) strictly related, one comprehensive answer is provided. We would like to thank the Reviewer for the kind and constructive suggestions. A revised version of the paper has been prepared that includes all requested modifications, and indeed focuses on the results of the effect of the morphology on soot particles activation experiments. For a detailed explanation, please see the answers to points (5), (6) and (25) of Reviewer#1. The Introduction and Results and Discussion sections are particularly affected by the re-framing of the paper. Exploring other theories of activation, unfortunately, is beyond the scope of the present work that instead aims to further develop kappa-köhler theory to account for effects (morphology, and chemistry of soot) not yet fully understood. Nevertheless, we acknowledge this suggestion as an interesting research direction for future developments that we will certainly keep as a perspective for future work.

(2) The study also suffers from limitations that include the important DMA transfer function effects and multiple charging (although noted on Page 17 by the authors, they do not go through more in-depth analysis), which is considered routine in established groups.

Answer. We would like to thank the Reviewer for the constructive suggestions and references. Indeed, including dve, multiple charges effects, DMA transfer function and kappa distribution is the proper way to treat the CCN activation data. In the revised version of the paper, the experimental data have been re treated to account for the above mentioned effects, and a morphology-corrected dve is then calculated, using the

Printer-friendly version

Discussion paper

data from TEM measurements. Furthermore, in the revised manuscript we updated the theory, the context of the presentation and all the figures. For more details on specific points, please see the answers to points (1), (2), (3), (4) and (6) of Reviewer#1.

Specific comments. (3) Page 2, Line 6: k-Köhler is not just for partially soluble particles, it's to address chemical complexity (mixtures of solutes of a wide range of molar masses) – and can account for partial solubility as well.

Answer. Corrected.

(4) Page 2, Line 9: Kohler theory is formulate for a particle. It can (and is) extended to a size distribution easily, as mentioned in the above texts. I don't understand why the authors present this as an issue.

Answer: We acknowledge that this could have been explained in a different and more appropriate way, and we thank the Reviewer for providing the pertinent literature references. Please notice that in response to this comment and to comments (1), (2), (3) and (4) of Referee #1, the Introduction and Theory sections have been entirely rewritten.

(5) Page 2, Line 10: Sure, you can use - and is even elegant - to use Dirac functions to represent many particles of a given size as a size distribution. I understand where the authors come from when they say that Kohler theory cannot be applied to a broad size distribution - but I also find it quite narrow because it is equivalent to saying that a size distribution with a finite particle width cannot be described with a monodisperse particle distribution (which is sort of an obvious statement)! On the other hand, Kohler theory can be applied to size distributions, even in the narrowest sense considered by the authors, because it defines the "size" above which all becomes droplets (this of course, assuming the soluble fraction is sufficient, with all that this implies). In this sense, a characteristic size is linked to a characteristic saturation - which is the basis of Kohler theory and the concept of a critical point that comes out of it.

Answer. We thank the Reviewer for this correction, in the revised version of the paper we updated the Introduction and Theory sections accordingly. Please also see answers to comments (3) and (4) of Reviewer#1.

(6) Page 2, Line 10: True, but then you need to use a theory that does not assume at least perfectly wettable particles. The work of Gorbunov, or adsorption activation theory can easily treat such situations – and is physically based. It would be nice if the authors actually refer to that work and consider it in their analysis.

Answer. Please see answer to comment (1).

(7) Figures: uncertainties are sometimes included in the activation plots, but they are not propagated later on in any of the analysis. This would be nice to see – and also include uncertainty from the DMA transfer function, shape factor, multiple charges, etc.

Answer. All missing uncertainties have been added to plots and tables.

(8) Page 19, line 30: I don't understand why nanoparticles will not be in equilibrium. The relevant timescale is extremely small – unless if I misunderstood the point raised by the authors.

Answer. Corrected. This sentence was not clear, and it has been removed.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-172, 2019.