

Comments on “Exploring the potential of the
nano-Köhler theory to describe the growth of
atmospheric molecular clusters by organic vapors”

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General comments

Manuscript explores the validity of the so-called nano-Köhler theory to describe the on-set of the growth of atmospheric particles. Although no simple answer to the question posed by the title is given, the manuscript provides a commendable effort in focusing on the validity of simplified assumptions often used—and too often overlooked—when modelling atmospheric cluster and particle processes; in this sense, the manuscript provides a natural continuation of the work performed earlier by some of the authors using the same methodology (ACDC cluster population model; Olenius and Riipinen, 2017). The presentation is clear and conclusions follow logically from the computational results (see, however, specific comments), although as a non-native English speaker I feel that usage of some additional commas could improve the representation.

However, even more (theoretical) insight could be obtained from the presented computational results, and the authors should consider including more detailed discussion on the manuscript.

- The premise of the nano-Köhler theory is that homogeneous nucleation of inorganic clusters is followed by activation of the same clusters by organic vapour condensation, while the results shown indicate that in actual atmospheric conditions the situation may not be so straightforward. In earlier studies using the same methodology (ACDC), the nature of the first step—formation of sulphuric acid–ammonia/amine clusters—has been found spontaneous, i.e. posing no thermodynamic

barrier, under some atmospherically relevant conditions. Likewise, results given in the manuscript for the ELVOCs (Sect. 4.1.2) seem to indicate barrierless condensation of organic vapour. Thus, it seems that there are four possible scenarios: i) thermodynamic barrier for both inorganic cluster formation (nucleation) and organic condensation (activation), ii) thermodynamic barrier inorganic cluster formation and barrierless condensation, iii) no thermodynamic barrier for inorganic cluster formation but thermodynamic barrier for organic condensation, and iv) no thermodynamic barrier for inorganic cluster formation nor organic condensation. It would be interesting to know how the number of thermodynamic barriers would contrast to the overall picture presented in Fig. 8.

- Related to the overall picture and schematics of Fig. 8, authors remark that “conditions for different growth mechanisms depend on vapor properties and environmental conditions and thus they cannot be generalized to arbitrary compounds and conditions”. However, as authors have performed simulations using two different scenarios for particle loss with different size dependencies, it would be interesting to know how sensitive this scheme is to the nature and strength of particle losses.
- Table 3 gives a good summary on different simulation sets, and it would help the reader if these would also be referred accordingly in Results and discussion.

Specific comments and technical corrections

- Page 1, line 27: ‘aerosol forcing’ → ‘aerosol radiative forcing’.
- Page 2, lines 1–12: The role of ions for the NPF process in addition to organic compounds and bases could be mentioned. Related to this, there is no reference corresponding to ‘Kirkby et al., 2016’ in the list of references.
- Starting from page 2, there are several references to articles ‘Kulmala, 2004’ and ‘Kulmala et al., 2004’ in the manuscript. However, only the one corresponding to ‘Kulmala, 2004’ is given in the list of references, although it should be ‘Kulmala et al., 2004’. The list of references has also other issues and should be revised by the authors.

- Page 3, line 11: Heterogeneous, not homogeneous, nucleation of the organic vapour should be implied.
- In relation to Eq. (1), a_{org} is used to denote the activity coefficient of the organic compound. As a is commonly used for the activity, this seems somewhat misleading. I would recommend using f_{org} for the activity coefficient, as γ has been already reserved for other use. Also, the surface tension in the Kelvin term should refer to the droplet/cluster as whole, not to the organic compound.
- Page 4, lines 17–18: It should be noted that if adsorption of vapour on the insoluble seed surface is taken into account, it is possible to have a maximum in the saturation ratio vs. cluster size curve [1].
- Page 4, lines 18–30: Although mainly phrased in terms of water vapour, theoretical and simulation results can be found from the literature focusing on the nucleation/activation-transition [3, 4, 5], some of which might be relevant for discussion here.
- Figure 1: This is a very good figure illustrating the differences between simplified nano-Köhler theory and the real system behaviour. However, the meaning of double-headed thin arrow in the real system description is not clear, does it imply forward and backward crossing of the thermodynamic barrier?
- Table 1: Is there any reason, why the condensing organic vapour has to be water-soluble in the nano-Köhler theory?
- Page 6, line 8: General Dynamic Equation (not Dynamics). Also, although this is a matter of taste, Eq. (2), when given in molecular resolution, could be referred as an extended Smoluchowski coagulation equation, considering Marian Smoluchowski’s seminal contribution to the theory.
- Page 6, line 15: An original reference [2] for the ACDC model should be given.
- Equation (3): Although containing the Kelvin term, this equation could be more properly referred as a condition of detailed balance than the Kelvin formula.
- Page 7, line 16: Mass of 500 amu is given here for the LVOC_{large}, while in Table 2 and caption of Fig. A6, 600 amu are given. Which one is right?

- Page 7, lines 26–29: Would there be other likely contributions, besides Raoult’s law effect for the organic vapour, from the inclusion of water vapour into simulations?
- Table 3 and page 21, line 5: The unit for pressure (Pa) is missing.
- Figures 2 and 5: Does the solid line indicate clusters with 1:1 stoichiometry? I could not find any explanation from the text.
- Page 19, lines 13–15: When considering Eq. (3), this is right when considering a given compound. However, as in general higher molecular mass implies smaller equilibrium vapour pressure, this statement sounds odd. It should be noted that the ratio $m_{\text{org}}/\rho_{\text{org}}$ in Eq. (3) refers to the (partial) molecular volume of the organic compound in the cluster, correlating strongly with the surface area of a (spherical) molecule at the surface. From this perspective, it might be better to rephrase the sentence pointing out the importance of molecular volume/exposed surface area instead of molecular mass on the equilibrium vapour pressure over a curved surface.

Additional references

- [1] A. Laaksonen and J. Malila, *Atmos. Chem. Phys.*, 16, 135–143, 2016.
- [2] M. J. McGrath, T. Olenius, I. K. Ortega, V. Loukonen, P. Paasonen, T. Kurtén, M. Kulmala, and H. Vehkamäki, *Atmos. Chem. Phys.*, 12, 2345–2355, 2012.
- [3] P. Mirabel, H. Reiss, and R. K. Bowles, *J. Chem. Phys.*, 113, 8194–8199, 2000.
- [4] H. Reiss and G. J. M. Koper, *J. Phys. Chem.*, 99, 7837–7844, 1995.
- [5] R. P. Sear, *Europhys. Lett.*, 83, 66002, 2008.