

Final response to referee comments on "Modelling Ag-particle activation and growth in a TSI WCPC model 3785" by F. Stratmann et al.

First of all, the authors would like to thank both reviewers for their time and effort. Thanks to their work, we will be able to present a clearer and better revised version of the original manuscript.

In the following, comments by both reviewers will be addressed in the order as their subjects appear in the text. Technical comments will be corrected in the revised manuscript, all specific comments on the contents of the manuscript are answered in the following and will (of course) find their way into the revised manuscript.

1. Comment: *p. 2219, lines 22 – 25: Reference of earlier theoretical and experimental work (Stolzenburg and McMurry, 1991; Saros et al., 1996) regarding the effect of high aerosol number concentration on vapor depletion should be included in the introduction.*

Reply: The reviewer is right, these earlier works will be mentioned in the revised manuscript.

2. Comment: *p. 2221, line 7: The only description of the model used for homogeneous nucleation is the Girshik et al. (1990) reference given here. There is also a reference to Fine Particle Model for FLUENT, but the user manuals and details of how homogeneous nucleation is handled in the model are not easily available at the Particle Dynamics web site. My concern is this: the Girshik formulation is well-known to produce rates that are about three orders of magnitude high (Du et al., Phys. Rev E, 79, 021604, 2009). The temperature dependence is not bad, but the rates are much too high. Are the authors aware of this? And does the Fine Particle Model for FLUENT scale the homogeneous nucleation rates to account for this known error? The acknowledgement of the error and its correction probably does not need to be in the body text of the paper, but maybe it should be included as a footnote?*

Reply: Girshik was used without correction here. One has to note that expressions other than Girshik might introduce errors even larger than three orders of magnitude. We have chosen a rate expression that we consider well-known and accepted.

3. Comment: *p. 2224, equation 9: It is unclear from the cited reference how the equation was derived. The quantity in the exponential also appears to be dimensionally inconsistent (having units of number concentration instead of being dimensionless). A definition/description of the nucleation time t should be given since it essentially determines how much the activated particle grows.*

Reply: This seems to be a misunderstanding, admittedly caused by not defining J_{het} more specifically. One has to note that J_{het} is the nucleation rate *per particle* and unit time, not per volume. The revised manuscript will be more specific on this issue.

The nucleation time is the time a particle spends in a control volume, i.e. the x-length of the control volume divided by the x-velocity of the flow through the control volume.

Since we are working with a laminar flow profile, other flow directions don't have to be considered. However, one has to remember, that the nucleation time is not of central importance: the steep rise of J_{het} turns the nucleation probability P virtually into a step function in which the exact value of the nucleation time is of only minor relevance.

4. Comment: *p. 2224, lines 5 – 7: It is unclear how the authors determine activation efficiency from nucleation probability, as the probability of activation depends not only on the vapor supersaturation field, but also on the radial concentration distribution of the incoming aerosol. A reference should be given that provides the necessary equations/models that were used.*

Reply: Heterogeneous nucleation probabilities were calculated for each control volume based on the local thermodynamic properties resulting from the coupled solution of eqs. 1 - 4. In the solution process, particles/droplets were *assumed* to be activated and able to grow when their nucleation probability was at least 0.5. This means that activation efficiency was *defined* based on nucleation probability, not derived.

5. Comment: *p. 2228, line 13: In Figure 5, why does the grown particle diameter increase with radial distance before dropping off for a given sampled particle size?*

Reply: We will answer this question in two parts:

a) concerning the drop-off: particles simply do not activate close(r) to the walls, compare fig. 2P for the same observation.

b) concerning the diameter increase with radial distance: this has a number of reasons. First of all, particle activation does not start on the central axis of the instrument. It starts (the exact location depending also in initial particle size) somewhere between the axis and the wall. This can be seen from the same figure 2P. Additionally, particles off the central axis travel somewhat slower through the tube than the ones right in the middle, thanks to the laminar flow profile, which gives them more time to grow.

6. Comment: *p. 2228, lines 17 – 21: This text suggests that the different final grown sizes of sampled 6 and 15 nm particles is due to vapor depletion by the larger particles. However, the difference in nucleation time for the two sizes can also affect the final grown size as larger particles are activated at lower supersaturations and therefore start growing earlier in the growth tube when compared to smaller particles.*

Reply: The referee is right. Figure 5a alone does not conclusively show the effects of vapor depletion since initially bigger particles activate earlier and have more time to grow. Vapor depletion is better depicted in figure 5b. The text in the revised manuscript will be re-written accordingly.

7. Comment: *p. 2229, lines 3-10: It appears that Fig. 6a is inconsistent with Fig. 5b. In Fig. 5b essentially all 15 nm particles are activated out to concentrations 10^6 cm^{-3} . In Fig. 6a, however, the light blue points are for a 15 nm concentration of 10^6 cm^{-3} , and these points show no significant growth (i.e., particles well less than 1 micron – the assumed detection limit). If this is not an inconsistency, it needs to be explained!*

Reply: Figure 6a shows data only for the center line of the instrument. Apparently the

transition from activation to partial non-activation takes place somewhere between 15nm seed particle concentrations of $1e5$ and $1e6$. Figure 6a thus only tells us that particles do not activate in a small volume around the center line. Obviously so small, that the resolution of figure 5b does not suffice to show the effect this has on total counting efficiency.

The referee is right that this can easily be seen as an inconsistency, that's why we will add above explanation in the revised version of the manuscript.

8. Comment: *p. 2229, lines 12-13: Summary point a) appears only to be true for small particles. If Fig. 6a is correct, the authors actually should see counting efficiency drop off for very high concentrations of 15 nm particles. In any case, the trend in Fig. 6a appears clear: as the size of the particles increases, vapour depletion might be expected to play a larger role. I see the results as very specific to the two sizes modeled – if that is not the case, the authors need to state that, and show why it is true for particles of all sizes.*

Reply: The referee is correct with respect to the exact wording of the original manuscript. In fact, going further than the referee, one has to point out that summary point a) is - strictly speaking - not even true for small particles: If we increase the number concentration enough, vapor depletion will effect detection efficiency sooner or later. What we meant to say in the manuscript is: for a monodisperse aerosol, particle number concentration does not affect counting efficiency up to a certain number concentration (which depends on particle size); after that, counting efficiency will in fact experience a sharp drop. To put it more bluntly: for *typical* particle concentrations, counting efficiency of a monodisperse aerosol is not affected. For very high concentrations on the other hand, efficiency limits are also set by limits in optical detection, that's why these high concentrations should be avoided anyways.

9. Comment: *p. 2230, lines 1 – 3: How does this theoretically determined temperature limit for homogeneous nucleation compare with the experimentally obtained limit? Such a comparison would be a meaningful check on model results.*

Reply: Since the model, as pointed out in the manuscript, should be considered half quantitative in any case (due to the nucleation rate expression used), such a comparison will not give us additional insight into the model results.

10. Comment: *p. 2230, lines 9 – 11: The use of the term “CPC counting efficiency” when describing particles generated through homogeneous nucleation of the working fluid is confusing since the counting efficiency should be referring only to sampled aerosol. A definition for “counting efficiency” should be provided.*

Reply: This is true in a way. Our intention, however, is to point out how "wrong" measurement results can become when homogeneous nucleation is involved. For this reason, we have decided to use the typical definition for counting efficiency (counted particles / particles that entered the instrument) even if - strictly speaking - defining a counting efficiency for an instrument that itself produces particles is not very useful.

However, to make clearer that this counting efficiency is not a real counting efficiency, we will re-phrase the last sentence of the second-last paragraph (p. 2231, 6-8) to:

In addition, in case of large supersaturations inside the WCPC, homogeneous nucleation of water vapour can produce a significant erroneous signal due to particle production inside the CPC and thus lead to large changes in the perceived counting efficiency.

11. Comment: *p. 2231, lines 11-16: The last sentence is a little vague. Maybe the authors could highlight the conclusion by giving 3-4 concrete examples. Possible situations to consider include 1) and urban area with large numbers of combustion particles; 2) a rural area experience a nucleation/particle growth event; 3) a clean rural/remote continental site; or 4) middle/upper troposphere; etc..*

Reply: The last paragraph will be changed to:

The results confirm that the counting efficiencies of CPCs are dependent on both particle and vapour chemical composition. Consequently, at least for nanometer particles, there is not a unique cut-off diameter nor a single counting efficiency. When considering the measurements of total particle number concentration in e.g. an atmospheric polydisperse aerosol particle population, the results imply that the counting efficiency of small, freshly nucleated particles, might be a function of the number and size of the pre-existing Aitken and accumulation mode particles, resulting in biased total number concentrations. This should be kept in mind when interpreting the atmospheric total number concentration data in cases when sub-10 nm particles are present in large quantities. These effects could be rather significant for example when considering new particle formation in an urban environment.