Interactive comment on "Flux induced growth ofatmospheric nano-particles by organic vapors" by J. Wang et al.

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In this manuscript the authors present an interesting mechanism affecting the very initial growth of particles in atmospheric new particle formation process. This mechanism, referred to as growth due to the diffusion in cluster size space, is included in classical nucleation theory and can be derived from the net flux of clusters in heterogenous nucleation of organic vapours. Diffusion in cluster size space is basically analogous to traditional molecular diffusion, which spreads the molecules against the concentration gradient in spatial coordinates. Diffusion in cluster size space occurs against the concentration gradient in cluster size coordinate and tends to widen the cluster mode along this coordinate. In principle, this manuscript is worth publishing in ACP, since the studied mechanism may have even a significant impact on the new particle formation processes. However, I find that the authors likely overestimate the overall significance of this mechanism on atmospheric new particle formation and CCN production or, at least, the uncertainties in their estimates are not expressed properly. Furthermore, I would like to see a bit more detailed explanation of the studied mechanism, its nature became clear for me only after reading the authors' answer (Wang et al. 2012) to the interactive short comment (Paasonen and Nieminen, 2012) and discussing them with my colleagues. Thus, before I can recommend publication of this manuscript, the answers to and likely some modifications based on the following comments are needed.

We appreciate the thoughtful comments and constructive suggestions from Dr. Passonen. We have modified the manuscript accordingly. Below we address each of Dr. Passonen's comments specifying where in the manuscript we have made changes.

My two main comments are:
1) The physical basis for the mechanism needs to be expressed in a bit more detail. If I understand it correct, the cause for the positive net flux of sub-Kelvin diameter clusters is that when some of the clusters reach the Kelvin diameter, their growth becomes more probable than their evaporation. Thus, these clusters do not (on average) return to sub-Kelvin sizes, leading to decreased evaporation flux and to positive net flux (since the condensation flux remains constant, as long as the concentrations of seed clusters and organic vapour remain constant). This should be clearly expressed (if correct), otherwise the reader may not understand why the strong negative gradient in cluster concentrations with respect to cluster size would lead to average cluster growth.

The reviewer is absolutely correct that once clusters reach the Kelvin diameter, their growth becomes more probable than evaporation, leading to a positive net particle number flux (i.e. net growth). However, the conventional approach suggests that sub-Kelvin clusters cannot grow through condensation. So the key point is how the sub-Kelvin clusters reach the Kelvin diameter, or why there is a positive net flux in the sub-Kelvin size range that could move these clusters to Kelvin size. We believe a more fundamental explanation is the strong negative

gradient in sub-Kelvin particle number concentration with respective to particle size under steady state. As we described in detail in the manuscript (page 22820 line 22 to page 22821, line 13), for an individual particle smaller than the Kelvin diameter, the per particle evaporation rate is greater than the per particle condensation rate, i.e., $\gamma_g > \beta_g$. Therefore it is more likely for the individual particle to evaporate than to grow. However, because of the strong (negative) gradient in cluster population with respect to size ($f_g > f_{g+1}$), the total condensation flux (i.e., $\beta_g f_g$) is greater than the total evaporation flux (i.e., $\gamma_{g+1} f_{g+1}$) and the resulting net flux is positive (i.e., $J_g = \beta_g f_g - \gamma_{g+1} f_{g+1} > 0$). This net forward flux induced by heterogeneous nucleation can move sub-Kelvin particles over the energy barrier and allow them to grow to Kelvin diameter and larger sizes.

2) When presenting the results of their calculations, the authors do not express clearly enough the assumptions made. As the authors mention in their answer to our interactive short comment (Wang et al., 2013) and in Methods-section of the manuscript (page 22817, line 26 – page 22818, line 1), they do not claim that the mechanism presented in this manuscript would be the only one producing Kelvin diameter clusters. However, for Fig. 1 the GReff is calculated from the total flux J (is J determined from the growth rate of larger particles?), after which GReff is divided to the conventional drift and the discussed diffusion term (is the value of GRdiff calculated from the last term on the right hand side of Eq. 4, or is it simply GRdiff = GReff – GRdrif t?). The size dependent growth rates presented in Fig. 1 are then used for estimating the values for the enhancement of new particle formation rate (p. 22822, lines 12-16). This seems to mean that the calculated enhancement of new particle formation rate is based on assuming that all the observed particles (i.e. the particles, from the formation rate of which J is determined) have formed from seed clusters by heterogenous nucleation of organic vapours. If that is the case, it should be clearly mentioned, in addition to Methods-section, at least when the numbers are presented in Conclusions and in Abstract, perhaps also in Results -section. The question is not whether the described phenomenon exists, it does, but of its strength: if there are other mechanisms forming Kelvin diameter and/or larger clusters, the concentration gradient of sub-Kelvin clusters becomes milder which reduces the impact of the studied mechanism significantly.

The total flux *J* is derived from the equilibrium cluster distribution and condensation rate β_g (Seinfeld and Pandis, 2006). GR_{diff} is calculated from the 2nd term on the RHS of equation (4). These are now clarified in the manuscript.

The enhanced of survival probability and new particle formation are estimated for the cases when new particles are formed from clusters by both condensation of sulfuric acid and heterogeneous nucleation of organic vapor (Page 22822, line 22 to Page 22823, line 9). This is now further clarified in sections of results and discussions, conclusions, and abstract. We agree there are also other possible mechanisms (e.g. Nano Kohler theory). Including these mechanisms may change the gradient in sub-Kelvin cluster distribution and the impact of the "diffusion in size space", which will be included in future studies.

The following more specific comments and suggestions arise from the above main

comments.

The authors should keep it clear through the manuscript whether they are discussing cluster growth or new particle formation as a whole. E.g saying that conventional approach underestimates new particle formation (Abstract, page 22816, line 14, and Conclusions, page 22824, lines 15-16) by some factor is rather obscure. The meaning of term "conventional approach" is intuitive when discussing the growth rates of sub-3 nm particles due to organic vapour condensation (conventional – no diffusion term, novel – with diffusion term). But what is the conventional approach for new particle formation? This diffusion is, as authors state, included in the classical nucleation theory. On the other hand, if the diffusion contribution is not taken into account in some other approach for new particle formation, some other explanation for the formation of Kelvin diameter particles has to be assumed instead: the conventional new particle formation approach cannot be simply growth of e.g. 1.2 nm clusters with conventional growth rate, because then Kelvin diameter clusters would not be formed. Furthermore, the authors say that also CCN production is underestimated with conventional approaches by factor up to 60. This sounds like the current estimates of CCN production were severely wrong according to the results in this manuscript. However, the estimates for CCN production are, typically, based on the parameterisations derived for the new particle formation rate that is observed, and the mechanisms leading to the observed formation rate are thus included, even though not specified.

We thank the reviewer for this thoughtful comment. Indeed, the new approach is clear when discussing the growth rate of sub-3 nm particles, but effect on new particle formation currently described in the manuscript is only realized when new particle formation is based on conventional growth of the newly formed cluster. We agree with the reviewer that NPF parameterizations are typically based on measurements, therefore the mechanism described here is implicitly included. To eliminate any possible confusion, we have revised the sentences in both abstract and conclusion to describe the impact on growth rate and calculated survival probability instead.

As the authors state (p. 22820, lines 12-14), the term for GRdiff in Eq. (4) does not depend on the actual values of fg but on its shape. This is true for the growth rate (which can describe the growth of 10000 or 1 or even 0.001 particles), but the flux J does depend on the values of fg: if there is a certain number of particles formed in the new particle formation process and they are all assumed to grow with the mechanisms presented in this manuscript, the numeric values of fg should be unambiguous. Thus, when the authors present the estimations of the significance of GRdiff on atmospheric new particle formation by example measurements, they should also present the values of fg(g) required for producing the new particle formation rates observed during the studied particle formation events. These concentrations should be compared e.g. to the measurement results by Lehtipalo et al. (2009) and Kulmala et al. (2013) in order to estimate whether the studied mechanism can explain the new particle formation event. Without doing this, or if the required cluster concentrations turn out to exceed drastically the observations, the authors should not suggest as high enhancement factors for new particle formation as they do.

For the case presented in Figure1, we calculated the sub-Kelvin cluster concentrations between 1.7+-0.2 nm, the beginning of the third size regime described in Kulmala et al. (2013). The observed growth rate within this size range was substantially higher than that predicted from condensation of H2SO4 alone, and organics are considered to contribute substantially to the total growth (Kulmala et al., 2013). If we assume the particle growth is dominated by heterogeneous nucleation of organics, to reproduce the reported average new particles formation rate (J_3) of ~0.5 cm^{-3} s^{-1} during the NPF events, the concentrations of clusters between 1.5 and 1.7 nm, and 1.7 and 1.9 nm are calculated as 5000 cm^{-3} and 250 cm^{-3}, respectively. The magnitude of the concentrations are broadly consistent with the average ~800 cm^{-3} for these size ranges reported in Kulmala et al. (2013). This comparison is now included in the results and discussions section. The comparison to Lehtipalo et al (2009) is somewhat challenging as the cluster concentrations within the above sub-Kelvin size ranges are not reported.

The effect of coagulation reducing cluster concentrations is not taken into account (page 22822, lines 20-21). Could the authors estimate the effect?

Effects from cluster scavenging by coagulation with background aerosol are not included in this paper, but early work on the multistate kinetics of nucleation in the presence of background aerosol (McGraw and Marlow, 1983) provides a model-tested criterion for when these effects are important. Empirically, it was found that the condition $A_{\mathrm{Fuchs}} / f_1 a_1 \approx 1$, here f_1 is the concentration of monomer, a_1 the surface area per monomer, and A_{Fuchs} the Fuchs surface area concentration of background aerosol, provides a good characterization of the threshold condition, below which cluster scavenging can be neglected, and classical nucleation theory, which is based on the same fluxes, i.e. condensation and evaporation, used in the manuscript, applies even with scavenging by background aerosol present. Beyond this approximate condition, e.g. as A_{Fuchs} is increased, the classical theory needs to be extended to include the scavenging loss. McGraw and Marlow (1983) present the full kinetics (condensation, evaporation, and cluster scavenging) using continued fraction extension of the classical Becker-Döring nucleation kinetics and developed the aforementioned condition from a consideration of time scales for nucleation and cluster scavenging (McGraw and Marlow, 1983). McMurry et al. (2005) introduced an equivalent dimensionless parameter, *L*, for a different purpose; namely, as a criterion for new particle formation in the sulfur-rich Atlanta atmosphere: New particle formation was typically observed when *L* was less than unity but not when *L* was greater. Combining of these independent findings suggests that when new particle formation is observed to occur i.e. $L \approx A_{\mathrm{Fuchs}} / f_1 a_1 < 1$, so that the time scale for nucleation is less than the time scale for cluster scavenging, the latter process can be neglected. Conversely when the scavenging rate is high, and needs to be included, it is unlikely that new particle formation will occur anyway. This is now clarified in the manuscript.

References

McGraw, R., and W. Marlow, W. (1983), "The multistate kinetics of nucleation in the presence of an aerosol", J. Chem. Phys. 78, 2542-2548.

McMurry, P. H., M. Fink, H. Sakurai, M. R. Stolzenburg, L. Mauldin, K. Moore, J. Smith, F. Eisele, S. Sjostedt, D. Tanner, L. G. Huey, J.B. Nowak, E. Edgerton, D. Voisin, 2005, "A Criterion for New Particle Formation in the Sulfur-Rich Atlanta Atmosphere," Journal of Geophysical Research – Atmospheres, 110, D22S02, DOI:2005JD005910.

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Technical comments:
In Abstract (p. 22814, lines 16-18) the verbs are in incorrect form: 'strong gradient…lead to…, and therefore driving'. This sentence is also otherwise long and fragmented.

The sentence is revised to:

"We find that the strong gradient in cluster population with respect to its size leads to positive cluster number flux. This positive flux drives the growth of clusters substantially smaller than the Kelvin diameter, conventionally considered as the minimum particle size that can be grown through condensation."

The sentence on page 22815 line 28 – page 22816 line 2 sounds strange: 'For 1-2 nm clusters, : : : Kelvin diameter would prevent condensation on these clusters.'

"For 1-2 nm cluster" is removed and the sentence is revised to:

"However, thermodynamic considerations suggest that the strong increase of equilibrium vapor concentration due to cluster surface curvature (Kelvin effect) would prevent ambient organics from condensing on these small clusters."

Page 22816 line 4 should be 'influences' instead of 'influence'.

Corrected.

Page 22818 line 19: The connection between dN/dDp and fg should be given explicitly.

Done. The sentence is changed to:

As $\frac{dN}{dD_p} = \frac{f_g}{\nabla_g D_p}$, rewriting …

Page 22819 lines 7-9: This analogy could be explained in a bit more detail: the gradient of concentration with respect to the size coordinate spreads the mode of the particles along the size

coordinate. Without this the analogy is clear in terms of the reason (gradient), but not in terms of the consequence (spreading).

Thanks for the suggestion. The following sentence is included:

"Similarly, this diffusion due to the concentration gradient spreads the cluster population along the size coordinate. The second term…"

Page 22820, lines 12-14: "Because fg appears in both the numerator and denominator, only the shape of the cluster size distribution is required to derive GRdiff .". This sounds like fg would disappear from the term for GRdiff in Eq. (4), which it naturally doesn't, but remains in the denominator of the term including dfg/dg resulting from the derivation.

We agree that f_g would not disappear completely from the terms for GR_{diff}. As was described in manuscript, the shape of cluster size distribution (f_g) is required to derive GR_{diff}. We have modified the text to:

Because f_g appears in both the numerator and denominator, only the shape of the f_g (i.e., steady state cluster size distribution) is required to derive GR_{diff}.

Page 22820, line 15-18: How is 'substantial' defined? In the next sentence it is said that (in this case) the minimum size of the particles that grow is overestimated by 20 %. This percentage corresponds to the 'substantial' growth rate occurring at 1.5 nm, mentioned in the previous sentence. However, as stated later on (page 22821, lines 14-15) also the particles smaller than 1.5 nm grow, although (on average) very slowly because the number of clusters in each size class is very high. Thus, giving a percentage for the minimum growing size is not reasonable, at least not in current form.

We have clarified the description and removed the percentage for decrease in the minimum growing size:

"As a result, the overall growth rate GR_{eff} remains 5% and 1% of the maximum growth rate (11nm/hr, occurs at 3.5 nm in this case) at sub-Kelvin D_p of 1.68 and 1.57 nm, respectively. This indicates that the conventional approach substantially overestimates the minimum size of the particles that grow through condensation of organics."

Fig. 3a and b. It is mentioned in the text (page 22821, lines 27-29), that the fractional differences between Dp;lower, Dp;upper and Kelvin diameter increase with decreasing Kelvin diameter. (Is fractional difference the correct term, does it mean their ratio?) However, in Fig. 3 it looks like the absolute difference between either Dp;lower or Dp;upper and Kelvin diameter is constant. Thus, I find the figure would be more informative if the y-scales would be linear instead of logarithmic.

The fractional difference refers to the relative difference (i.e., (x-y)/y), and is now clarified. The absolute differences also increase with decreasing Kelvin diameter, albeit less pronounced. For example, the absolute difference between $D_{p,lower}$ and $D_{p,upper}$ increased from 0.5 nm to 0.8 nm as Kelvin diameter decreased from 2.9 to 1.4 nm in Figure 3b, and increased slightly from 0.6 to 0.7 nm as Kelvin diameter decreases from 3.9 to 1.6 nm in Figure 3a. The relative changes in diameters likely better reflect the impact on growth rates and survival probability. For example, for an absolute difference of 1nm between $D_{p,lower}$ and Kelvin diameter, the impact on particle survival probability would likely be more significant when Kelvin diameter is 2 nm ($D_{p,lower}$ = 1 nm) than that when Kelvin diameter is 4 nm ($D_{p,lower}$ = 3 nm). Therefore, the y-axis is plotted in logarithmic scale.

Page 22821 lines 2-7. These two sentences are a bit misleading: it is said that the strong negative gradient causes positive net flux, which can effectively grow clusters over the Kelvin diameter. If there is a negative gradient in concentrations, even not strong one, a positive flux is produced because some clusters grow over the Kelvin diameter (because the mode is lognormal, it has a positive value at all size classes, even though it is very small in larger sizes). Whether the growth is effective or not, depends not only on the gradient but also on the cluster concentrations and the size difference between seed cluster and Kelvin diameters.

We have removed the word “effective” from the sentence. These descriptions are intended for explaining the mechanism responsible for the growth of sub-Kelvin particles. In the following paragraph in the manuscript, we describe the size ranges at which the contribution from the concentration gradient is substantial.

Page 22824, line 8: I find that starting this sentence with ”In addition,...” doesn’t give correct relation for this and the previous sentence. The latter sentence is (at least partly) the reason for the previous, not a separate result.

Thanks for the suggestion, we have removed “in addition” and reversed the order of the two sentences.

References:
Lehtipalo, K. et al.: Analysis of atmospheric neutral and charged molecular clusters in boreal forest using pulse-height CPC, Atmos. Chem. Phys., 9, 4177-4184, doi:10.5194/acp-9-4177-2009, 2009.
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