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Atmospheric Chemistry and Physics Discussions

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

Ph.D. Paasonen (Referee)

pauli.paasonen@helsinki.fi

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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.

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.

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 GR_{eff} is calculated from the total flux J (is J determined from the growth rate of larger particles?), after which GR_{eff} is divided to the conventional drift and the discussed diffusion term (is the value of GR_{diff} calculated from the last term on the right hand side of Eq. 4, or is it simply $GR_{diff} = GR_{eff} - GR_{drift}$?). 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 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.

As the authors state (p. 22820, lines 12-14), the term for GR_{diff} in Eq. (4) does not depend on the actual values of f_g 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 f_g: 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 f_g should be unambiguous. Thus, when the authors present the estimations of the significance of GR_{diff} on atmospheric new particle formation by example measurements, they should also present the values of $f_g(g)$ 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.

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

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

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

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

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).

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

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.

Fig. 3a and b. It is mentioned in the text (page 22821, lines 27-29), that the fractional differences between $D_{p,lower}$, $D_{p,upper}$ 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 $D_{p,lower}$ or $D_{p,upper}$ and Kelvin diameter is constant. Thus, I find the figure would be more informative if the y-scales would be linear instead of logarithmic.

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.

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.

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.

Kulmala, M. et al.: Direct Observations of Atmospheric Aerosol Nucleation, Science, 339, 6122, 943-946, DOI: 10.1126/science.1227385, 2013.

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Interactive comment on Atmos. Chem. Phys. Discuss., 12, 22813, 2012.