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

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We thank Passonen and Nieminen for their comment on our paper. They acknowledge the correctness of the theoretical derivation for the proposed flux-induced growth term, but express concerns over the appropriateness of interpretation and use of this term to modify the conventional growth law for estimating new particle formation rate, e.g., to estimate the subsequent production of cloud condensation nuclei. The comment raises two issues, the first of which concerns the mechanism of new particle formation. To simplify discussion in the paper we employed a heterogeneous nucleation model and a single, model organic, condensable vapor to frame our argument while estimating the growth rates of particles from sub-Kelvin particle diameter to larger sizes. The second issue concerns our use of standard homogeneous/heterogeneous nucleation

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boundary conditions and assumption of a steady state nucleation rate.

Mechanism: Uncovering the principal molecular pathways and mechanism(s) responsible for atmospheric new particle formation remains an important goal of field study, but is not the main purpose of our paper. Our objective is to replace the conventional growth rate (Eq. 1) with an improved expression (Eq. 4) that describes the process better by including a flux-induced growth term that allows for barrier crossing. To simplify discussion we employed the same model assumptions already behind the conventional Eq. 1, referring to, e.g., concentrations of a (single) condensing species far from and at the particle surface corrected in the same way, through the Kelvin relation, for curvature. Later refinements might well include lumping together multiple organic species into a single effective compound. To some extent our choice of model parameters already attempts to do this. There are two terms in Eq. 4. One of these, the drift term, looks much like the conventional growth term from Eq. 1 (compare the black and blue curves of Fig. 1). We added the second term, from nucleation theory, which results from diffusion along the coordinate of cluster size and is essential if one is to account for barrier crossing. Neither heterogeneous nor heteromolecular homogeneous nucleation can occur without it because the conventional growth law (Eq. 1) predicts negative growth below the critical Kelvin cluster size. We rewrote this term in the paper, converting it into an equivalent diffusive flux that appears in Eq. 4 and generates the green curve of Fig. 1. When combined with the conventional term, the red curve of Fig. 1 results. (The use of “flux” appears to be more standard in atmospheric chemistry and physics than the concept of “diffusion along a coordinate of cluster size” and provides a natural framework for extension of Eq. 1). The model of clusters growing due to condensation of a single vapor was chosen for expediency and the fact that this is the same model that stands behind conventional calculations of growth rate based on Eq. 1. A more realistic model might well have included multiple condensing species (e.g. sulfuric acid and water, or sulfuric acid, organic acid and water). But even for these more complex mechanistic schemes, a very similar picture to the barrier crossing schematic of Fig. 2 would emerge in a quasi-unary representation of heterogeneous nucleation similar to the representation of binary [1] and ternary [2] nucleation mechanisms. Given the difficulty of measuring the composition of particles at a few nanometers, it is very difficult to provide “direct” evidence for a particular mechanism. We do not claim that production of clusters with Kelvin diameter is solely caused by heterogeneous nucleation described in the paper, or heterogeneous nucleation is the only mechanism that allows the growth of small clusters by organic compounds despite the very strong Kelvin effect. As we describe in the manuscript: “*Here we don’t attempt to dispute or ascertain the relative importance of various mechanisms for the early growth of nucleated clusters described in previous studies. Instead, we focus on an alternative mechanism that has not been considered. . .*”. Our paper is more a process study than it is an attempt to formulate a detailed mechanistic model of new particle formation. A theoretical investigation has to start somewhere and a sensible strategy is to make improvements to important model components, as we have done here for the particle growth rate, before the whole integrated process can be constructed. Recent measurements [3] and theory [4] have shown that particles in the nano-size regime activate significantly below the Kelvin size. The present paper focuses in more detail on how this sub-Kelvin activation occurs through flux-induced growth – the same “driving force” that enables condensation particle counters to detect particles substantially smaller than the Kelvin diameter [3].

The second issue raised in the comment concerns our assumption of a steady-state flux rate and use of boundary conditions borrowed from nucleation theory. The justification here is that the lifetime of transients during heterogeneous nucleation described in the manuscript is fast compared to the time scale for the variation of condensing organics concentration. Using the method from Shi et al. [5], we calculate, for purposes of this response, a value of 87s for the characteristic time to reach steady state using the parameters from Table 1, which is substantially shorter than the typical time scale for variation of organic vapor concentration or the initial cluster (i.e. seed) population. This is similar to the rapid decay of transients and attainment of steady state (i.e., on the order of seconds or even less) for homogeneous nucleation of sulfuric acid water system [6] or when a ternary species such as ammonia is incorporated in the nucleus [7].

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