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Interactive comment on "Influence of aerosol lifetime on the interpretation of nucleation experiments with respect to the first nucleation theorem" *by* S. Ehrhart and J. Curtius

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We thank Robert McGraw for the comments and suggestions.

RC: Ehrhart and Curtius (E&C) examine relative sensitivity of steady state nucleation rate to changes in vapor phase sulfuric acid concentration: d log J / d log[H2SO4] . In the case of unary (or pseudo-unary) homogeneous nucleation the flux, J , is constant along the growth coordinate, and the dimensionless relative sensitivity, also constant, may be interpreted (via the nucleation theorem) as being close to the number of molecules of acid present in the critical nucleus, n*. Under these idealized conditions

the nucleation theorem provides a remarkably useful tool that allows one to determine the molecular contents of critical nuclei directly from measurements of relative sensitivities of J with respect to the concentrations of the various condensable vapors present in the gaseous phase. E&C allow for cluster loss along the growth sequence due to collisions with the background aerosol and/or chamber walls that are always present to some extent in field or laboratory measurements. With significant loss both J and relative sensitivity depend on cluster size. E&C examine the steady-state flux, Jd , for growth through diameter d, and report on the relative sensitivity of Jd to acid concentration-equivalent to giving an apparent critical cluster size, nd* (here the number of acid molecules present in the critical cluster) as a function of scavenging rate (equivalently, cluster lifetime) and flux-through diameter, d. Their results, based on simulations with the SAWNUC microphysical aerosol nucleation model, include the finding that nd * can vary widely for identical nucleation conditions but different loss rates, thus obscuring inference of molecular content based on the nucleation theorem. Similar results were obtained independently (Malila et al., 2013; 2011) using an analytic expression for nucleation rate that is a closed-form generalization of the Becker Döring kinetics to include cluster loss (McGraw and Marlow, 1883). Relative sensitivities can be obtained simply, from this expression, by evaluating log Jd at nearby values of log[f1]and obtaining the slope, where f1 is condensable monomer concentration. Our findings, based on Malila et al. (2013, 2011) and unpublished calculations, are that for d > d* (d < d*) the apparent critical size becomes increasingly larger (increasingly smaller) than the actual critical size with increasing cluster loss rate. For d ≈ d* there tends to be a persistence of near equality between nd* and n* but ultimately departure, one way or the other, sets in with still further increase in loss rate. E&C demonstrate the cases d > d* and d ≈ d*, and it would interesting for them to also confirm whether or not a reduction in apparent critical size occurs within the SAWNUC model for subcritical numbers of molecules present in the neutral cluster. Indeed the last sentence of their paper seems to call for just such a study.

AC: SAWNUC includes subcritical clusters. In the system studied here we did not find

a significant decrease of n* for subcritical cluster with decreasing lifetime.

RC: From the perspective of its early thermodynamic roots, one can easily be led to the view that interpretations based on the first nucleation theorem are sufficiently obscure and/or so fragile as to have little practical utility in the "real world" wherein cluster losses can be significant and multiple routes to stable particles may be present at the same time. Fortunately, more recent kinetic extensions of the nucleation theorem, beginning with the work of Ford (1997), are providing new insights into the relative sensitivity that extends its interpretation to higher-order derivatives and its utility to more complex chemical kinetic nucleation mechanisms and multipath systems (McGraw and Wu, 2003). For example, McGraw and Zhang (2008) examine the very case discussed by E&C in their conclusions, namely, ternary nucleation that competes with binary nucleation. It was found using the multipath approach that the overall sensitivity for this case is simply the flux-weighted average of sensitivities along the two (binary and ternary) pathways. In the limit that one path prevails the expected binary or ternary slope results, while in the transition regime, where both pathways carry significant flux, there is a high amount of curvature as the slope is a changing (but still well defined) flux-weighted linear combination of its limiting values (McGraw and Zhang, 2008).

AC: We included these references in the conclusion.

RC: 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 effects from cluster lost require modification of the Becker-Döring nucleation kinetics and, accordingly, of the nucleation theorem. Guided by an examination of characteristic time scales, it was found that the condition $A / (f_1 s_1) \approx 1$, where f_1 is the concentration of monomer, s_1 the surface area per monomer and A the surface area concentration of background aerosol, provides a good characterization of the threshold condition, below which (e.g. for smaller A, or for larger f_1) cluster scavenging can be neglected, and the Becker-Döring kinetics applies even with scavenging by background aerosol present. Exceeding this approximate equality, e.g. as A is increased, the Becker-Döring kinetics

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needs to be extended to include the cluster loss. McGraw and Marlow (1983) include condensation, evaporation, and cluster loss, but only considered this detailed kinetics out to about twice the critical cluster size. McMurry et al. (2005) introduced an equivalent dimensionless parameter, $L = A_{Fuchs} / (f_1 s_1)$, for a different purpose; namely, as a criterion for new particle formation (specifically, for the formation of particles that exceeded 3nm diameter in the sulfur-rich Atlanta atmosphere): New particle formation was observed when L was less than unity but not when L was greater. (For scavenging of nanoparticles $A \approx A_{Fuchs}$.) Combining these very different findings suggests that when new particle formation is observed to occur in the field i.e. $L \approx A / (f_1 s_1) < 1$, so that the time scale for nucleation is less than the time scale for cluster scavenging, the latter process can be neglected in the theory. Conversely when the scavenging rate is high, and needs to be included in the theory, it is unlikely that new particle formation will be seen in the field anyway!

AC: We agree with that and wrote in the conclusion a sentence pointing to this but with the argumentation based on lifetimes and characteristic time to grow to detectable sizes. We included a paragraph on that topic now in the results section together with the references.

RC: In their conclusions, E&C remark that the introduction of a sink is mathematically similar to introducing a small but significant evaporation term to all clusters. This is an interesting perspective but the authors should be more explicit in what they mean. Because the barrier can always be expressed in "kinetic potential" form as an extended product of evaporation to condensation rates (Wu, 1997), adding to the evaporation terms, alone, would seem to simply heighten the barrier; fluxes along the growth sequence would still be conserved. This is not similar, mathematically or physically, to having cluster loss along the growth sequence.

AC: From the view of an experimentalist who determines n* just from the particle formation rates, the effect of a wall loss is indistinguishable from the effect of having higher evaporation rates.

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RC: The left-hand-side of Eq. 3 needs a small correction (+2 if clusters are defined as in classical nucleation theory, or +1 if the clusters are defined so as to satisfy the law of mass action - the distinction derives form the 1/S correction due to Courtney, where S is saturation ratio, as cited and described in McGraw and Wu, 2003).

AC: We changed eq. 3 and added a clarification.

RC: To conclude, this is a useful and well-written paper that is likely to spark debate on the utility of nucleation theorems. I look forward to the authors response to the comments made in this review.

AC: Thank you.

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