

## ***Interactive comment on* “Laboratory studies of ice formation pathways from ammonium sulfate particles” by M. E. Wise et al.**

**Anonymous Referee #1**

Received and published: 8 September 2008

### **General comment**

The authors did not respond to my initial comments in a form that gives me any confidence that the technique for studies of deposition ice nucleation is sound. I find no basis for their assumptions and measurements for attributing the conditions of the onset of deposition ice nucleation. My opinion is that the paper should be withdrawn and rewritten to focus on those parts of the study that can be fully supported.

### **Some specific responses to author comments (previous comments italicized)**

*Primary reviewer 1 comment: The paper takes a method that, with care, is useful for qualitative indication of ice formation by liquid particles under specific compositional and temperature conditions and violates its primary useful principle to try to apply it*

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toward measuring deposition ice nucleation.

*Author response: We believe that the flow tubes are useful for the quantitative indication of ice formation from liquid particles.*

Although the authors chose to focus on my own casual and poorly considered use of the word qualitative, they follow with a very general and overarching statement. They should note that my statement mentioned the ability to determine specific compositional and temperature conditions. The literature is quite clear on the fact that the determination of proportions of particles nucleating requires special calculation/simulation. I will not enter arguments about other methods or comparisons amongst methods.

*...include for the first time studies of depositional nucleation using the flow tube. Since this has never been done before, it does not seem valid to simply dismiss the technique as invalid. We do not agree that it violates any principle.*

My comments do not represent simple dismissal. Instead, they are very critically focused. They are driven by experience with low temperature phase transition systems and numerical simulation of these. I find simplistic assumptions made in developing this new method for flow tube study of deposition nucleation, whereas a rigorous examination is needed.

*Primary reviewer 1 comment: The basic first problem I see in the present paper is that I do not believe that the authors have truly resolved the RH to which fully dry particles are exposed in the transition of air between the conditioning and observation tubes in their experiments to confirm the role of deposition nucleation on ammonium sulfate.*

*Author response: The major problem reviewer 1 has with the manuscript is the method in which we determined the ice saturation ratio ( $S_{ice}$ ) in the flow tubes during depositional ice nucleation experiments. Without using numerical modeling studies (which the reviewer suggests that we do), we have the burden of proving that our experimental measurements determine  $S_{ice}$  correctly. In order to determine  $S_{ice}$  correctly, the vapor*

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*pressure in the observation region must be known with certainty. We have shown that the hygrometer correctly measures the vapor pressure created by the ice in the conditioning region (line 273). Therefore, we are confident that the hygrometer correctly measures the vapor pressure exiting the observation region.*

The hygrometer appears to be correctly measuring the vapor pressure at the bottom of the observation region. My key point, which is that the value of relative humidity in the transition between conditioning and observation regions (what the nuclei will respond to) is not resolved, is not addressed in this response. The burden of proof is indeed on the authors. The paper gives this critical point no consideration. I also do not consider it an unusual request to include numerical consideration of the dynamics and thermodynamics of the experimental system. This already has some precedence within the specific field of flow tube applications (see, e.g., Khalizov et al. 2006; also see <http://www.science.uwaterloo.ca/sloanj/LabAerosol.html>).

*The question then remains whether or not we are measuring the vapor pressure in the correct portion of the flow tube system. The reviewer inspired us to answer the question of whether measuring the vapor pressure from the observation tube exit was valid. Therefore, a new experiment was performed in which Sice was measured halfway down the observation tube. Given our experimental setup, this position was as far away as possible from the exit of the flow tube apparatus. In this experiment, the conditions of one of the heterogeneous ice nucleation experiments conducted in the original manuscript were duplicated. Sice was then measured at the flow tube exit and at the middle of the observation region. It was found that the Sice calculated at the flow tube exit was less than 5% different than that reported in the original manuscript. Sice measured at the middle of the observation region was less than 5% higher than that measured at the flow tube exit. Therefore, it was not high enough to change the conclusions of the original manuscript.*

The question remains whether vapor pressure is being measured as appropriate to where nucleation ensues. It seems clear that it is not. The new experiment sheds little

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light on the matter yet seems to indicate “higher values” at the tube midpoint, which alone emphasizes my point. The real questions: Where does nucleation ensue? What has the RH relaxed to at this point? What is the temperature at that point? Where in the 3-dimensional space does this occur? I do not think the authors know the answers. Simple considerations of the temperature transition suggest that the real action occurs in the transition between tubes and in the entry portion of the observation region. I explored some numerical calculations using a flow chamber model (Plooster, 1985). This combined microphysical/flow model indicated a symmetric situation, but a highly heterogeneous distribution of temperature and supersaturation in the first 20 cm of the observation region. Since I have no idea how to exactly set the initial temperature and humidity profile of air entering the observation region (and it matters), I hesitate to show any simulation results. Nevertheless, the results qualitatively follow my expectations. Since the air is warmer and with higher vapor pressure suddenly entering a region with colder side walls and parabolic flow, the transient highest supersaturation is not necessarily generated in the center of the tube but in lobes around this midpoint. These lobes may be focused within a small horizontal cross-axis distance of less than 0.5 cm in which some particles may deliquesce and freeze, with much drier air on either side for which particles would remain crystalline. The transition happens quite suddenly over a narrow temperature range. A colleague attempted a computational fluid dynamics simulation, which calculated even higher supersaturations and focusing of particles due to perturbations in the flow profile. Nevertheless, accurate application of a computation fluid dynamics model requires specific knowledge of the tube geometry, temperatures, and boundary conditions, including the transition region between the two tubes (Khalizov et al. 2006). I do not have that information.

*Reviewer 1 comment: What should be measured at the base of the observation tube, within the uncertainty of measurements, is ice saturation.*

*Author response: We experimentally determined the value of  $S_{ice}$  with the hygrometer. The procedure is explained starting on line 250.*

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Within the uncertainty of RH measurement at these temperatures, I believe there is no basis for believing it is much different than the ice saturation RH. It would be useful to know what value of RH was measured at this point in experimental conditions under which ice formation was not detected. Also, what value is measured there in experiments for which strong ice formation is detected? Is it ever any different?

*Reviewer 1 comment: Furthermore, why would such a large temperature difference between the conditioning and observation tubes be required to achieve such a low RH for ice activation if the particles cannot take up water?*

*Author response: There is a large temperature difference because water vapor is condensing on the tube walls (not onto the particle surface). This is explained on line 405, Sice could not simply be calculated using the temperature of the two cells because water vapor was lost to the walls of the observation region. This is because the observation tube walls were much colder than the conditioning region. Thus water vapor pressure must be measured directly using the hygrometer.*

Water does condense onto the particles at some point. How can one be sure this happens after all of the water vapor has been removed to the walls such that the steady-state vapor pressure far away at the tube exit has any relevance? I think it will be a very dynamic process in the design of this experiment, one that is not resolvable. The authors have not considered the realism of measuring the vapor pressure after transit of air through the critical region, which goes back to the burden of proof point.

*Reviewer 1 comment: Simple considerations suggest to me that the air enters the observation flow tube and achieves a transient high supersaturation (probably nonhomogeneous) that could even lead to water condensation and homogeneous freezing in an unknown proportion of the particles.*

*Author response: We agree that when the air enters the observation flow tube a transient higher supersaturation value is reached. However, we do not believe that water has condensed on the particles. The IR spectra do not show that the particles have*

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*deliquesced. Thus homogeneous freezing could not have occurred in an unknown portion of the particles. Furthermore, we do not believe that ice particles homogeneously condense from the water vapor in observation region. Without particles present we have never seen ice appear in the IR spectra.*

I believe that the authors are mistaken to imagine this as a simple one dimensional problem. It is a complex, three-dimensional heat and mass transfer problem. The measurements made away from the key region or integrated over the observation path may therefore give no inference to the history of what has taken place. If the authors would give serious consideration to the fluid dynamics and thermodynamics in the entry region, I feel they would understand this. One cannot imagine a homogeneous distribution of conditions in the transition region. The region of supersaturation can be strong and highly focused in ways that it may not be in the presence of a large population of liquid aerosols (standard method of operating the flow tube). The consequence could be that some particles will be exposed to a vapor pressure that leads to water uptake and freezing, while most others can remain dry. If one acknowledges that a transient supersaturation occurs, it is already assured that the particles will be involved in ice nucleation and then additional potential impacts on the water vapor and flow fields.

## References

Plooster, M. N., Computer models for simulation of experiments in the Atmospheric Cloud Physics Laboratory (ACPL). Rep. 5-31701, Denver Research Institute, University of Denver, Denver, CO, 78 pp, 1985.

Khalizov, A. F., M. E. Earle, W. J. W. Johnson, G. D. Stublely, and J. J. Sloan, 2006: Modeling of flow dynamics in laminar aerosol flow tubes. *J. Aerosol Sci.* **37**, 1174–1187, 2006.

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Interactive comment on Atmos. Chem. Phys. Discuss., 8, 15101, 2008.

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