

Interactive comment on “Homogeneous nucleation of sulfuric acid and water mixture: experimental setup and first results” by D. Brus et al.

D. Brus et al.

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We thank to reviewers for constructive review of our manuscript, we do also appreciate reviewers' suggestions to improve the manuscript.

Report of referee #1

Referee#1:

This paper adds to the list of experiments/results that have been presented over the decades. It has been improved from that originally submitted but questions remain on the techniques and measurements (listed below.) Whether it should be published

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depends on their answers.

The English also needs work (e.g. p. 23876 singular-plural on l.5, sentence fragment on l.19; 'of' vs. 'from' on l.1 and missing article 'a' in l.16,17, next page. Missing article 'the' in l.26, 27 p. 23879.).

Authors:

This will be corrected in new version of the manuscript.

Referee#1:

(i) Laminar flow tube. The name given to the overall apparatus could be a little misleading because (1) a warm gas flowing into a region with cooled walls will experience natural convection (buoyancy) and (2) the entrance of the cooled tube likely has some regions where the flow is not even steady with time. The authors should add a section or at least a few sentences discussing the likely flow profiles in the various regions of the flow tube. Typical Reynold's and Grashof numbers should be presented.

Authors:

Yes, we do agree with referee, the laminar profile in our tube is fully developed after 50 cm from the beginning of the nucleation chamber, where the temperature of the stream starts to reach the temperature of inner surface, see figure 3 of the manuscript. The expression “laminar flow tube” will be omitted in the whole manuscript; we will use only “flow tube” in new version of the manuscript. The typical profiles of Reynolds (Re), Grashof (Gr) and Archimedes (Ar) numbers at the axes as a function of the nucleation chamber distance are presented in inserted figure 1. The first 50 cm are influenced by buoyancy driven convection ($Ar \gg 1$), after 50 cm in the nucleation chamber starts to dominate forced convection ($Ar \ll 1$).

One short paragraph will be added to experimental setup section of the manuscript.

Referee#1:

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(ii) The use of filters in the experiment is an area of concern. (iia) HEPA filters can elute some vapors depending upon materials while the Teflon filter inside the apparatus, that needed an 'autoclaving' (probably not a correct usage here) cleaning procedure, is particularly troubling. How do the authors know about its final state of cleanliness? The use of polymer filter materials at elevated temperatures (~ 200 °C) does not seem to be a good idea. Was a glass wool or fiber filter found to be inadequate (much less likely to introduce contaminants?) Also, the temperature and location of the internal Teflon filter are unclear.

Authors:

In our system, the air flow is first passing via active black carbon filter to remove chemical impurities and then via HEPA filter to remove particles. When the experimental apparatus is running with heated furnace and without injecting the sulfuric acid solution (or pure water), the particle count shows values ~ 0 particles/cm³. The Teflon filter is used to remove residual particles from imperfect evaporation of liquid H₂SO₄. The filter itself helps us only to extend nucleation rates to lower values; the smaller background particle count is obtained.

The Teflon filter (MITEX Millipore 5.0 μ m LS) is stored in laboratory environment, so the autoclaving inside the apparatus is only way of its sterilization. The declared maximum operating temperature of Teflon filter used is 260 °C. The temperature inside the furnace is usually ~ 470 K (~ 200 °C). Any thermal decomposition of Teflon filter would be clearly observable in rise of particle count. When the Teflon filter is autoclaved the particle count reaches zero.

According to the Master Thesis of Yrjö Viisanen (1988) [Yrjö Viisanen: Binäärin nukleation tutkimiseen soveltuvan koelaitteiston kehittäminen: Rikkihapon ja vesihöyryn seos, Pro-gradu-tutkielma, University of Helsinki, Department of Physics, 1988], several types of filters were tested, and the MITEX Teflon filter was chosen as the best-one for its temperature and chemical stability (tested up to 260 °C).

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Any kind of impurities introduced into experimental system would appear in particle count or would be evident from Ion Chromatography analysis if their concentration would be higher than their detection limits (~ 0.02 mg/l).

Teflon filter is placed on the perforated Teflon support pad just after the furnace and before the entrance to mixing unit. The exact location and the legend will be added in to figure 1 of the manuscript.

Referee#1:

(iib) Since the H₂SO₄ vapor concentration for the final results are ultimately derived from losses obtained from the IC measurements, it seems another source of H₂SO₄ could be used. The hot filter might be unnecessary if the jet is not used, and cleanliness of the system could be bolstered.

Authors:

Yes, we plan to use saturator with 95-97% sulfuric acid in our future measurements. The basic advantage of using evaporation of the jet is that the prepared solution of sulfuric acid and water is very diluted and the concentration of sulfuric acid is constant in time. This also means that the demands for materials used are not so critical.

Referee#1:

(iic) There are a few lines on p.23879 that are troubling. It seems that a new filter must be used to measure again nucleation at the low H₂SO₄ (high RH) conditions. The reason given is that the walls of the instrument become a source of sulfuric acid vapor. But this is not a satisfying explanation. The walls of the cooled tube cannot be a significant source because the vapor must be highly supersaturated with respect to the bulk (i.e., acid solution on the walls) for nucleation to occur. If the 470 K (or mixing) region is an 'additional' source of H₂SO₄, then the IC measurements can pick that up. It is suggested that data from a rerun at high RH without changing filters and replacing mass balance with IC measured H₂SO₄. These results should be in agreement with

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the previous run. Hopefully, the Teflon filter did not become 'degraded' by the hot and acidic conditions it experiences over the course of the experiment. Sulfuric acid at 470 K and low water vapor can lead to SO₃ which can be very reactive towards plasticizers or even the plastic itself.

Authors:

The filter does not have to be changed to measure nucleation rates at low H₂SO₄ concentrations and high relative humidity. The part describing "a typical experiment" is optimized procedure that saves necessary experimental time. When we conduct are experiments backwards from high concentrations of sulfuric acid to low ones it just increases the time necessary for stabilization, we obtain reverse curve (exponential decrease) to that presented in figure 5. It takes about 6 hours for particle count to stabilize to plateau values. We made many crucial experiments concerning Teflon filter, it is very stable, and the results are reproducible even if we do not change it for long time (several weeks of continuous measurements).

Referee#1:

(iii) Plateau in particles is not well demonstrated for the 10 % RH data (23881, l10.)

Authors:

The particle count for the 10 % RH data is changing from 244 particles/cm³ (at 4:00) to 453 particles/cm³ (at 22:00), which is factor ~ 1.85 in 18 hours. With regard to duration of the experiment we consider it to be very stable.

Referee#1:

(iv) Three ways to count particles are discussed and they seem to not agree (the PHCPC results did not agree with 3025A in an early version of the paper and now they are not being compared.) Details for results that are shown need to be presented: charging efficiency assumed for DMPS system; was the effluent from DMPS neutralized before the 3025A? Certainly the DMPS using a given detector should agree with

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the detector deployed without the DMPS.

Authors:

The PHCPC was used only to determine nucleation zone. The UCPC TSI 3025A was found unsatisfactory for that purpose, p.23882, line 25, so we did not make any mutual comparison of PHCPC and UCPC TSI 3025A in nucleation zone experiment.

The DMPS measurements discussed in this manuscript are made using a bipolar diffusion charger (Ni 63) to achieve a steady state charge distribution (e.g. Liu B. Y. H. and Pui D. Y. H.: Electrical neutralization of aerosol, J. Aerosol Sci., 5, 465-472, 1974). Charging efficiencies are calculated according to Wiedensohler's parameterization (Wiedensohler A.: An approximation of the bipolar charge distribution for particles in submicron size range, J. Aerosol Sci., 19, 387-389, 1988), the charging probability of three nanometer particles is 0.02 and 0.03 for positive and negative charge, respectively. The inversion of raw data obtained from DMPS measurements is applied to obtain final distributions and total count. Because the inversion itself introduces uncertainty into results we compare them with raw data of stand-alone UCPC TSI 3025A, where we do not take into account counting efficiency and losses, p.23882, line 15. To successfully match the DMPS total count, the counting efficiency of UCPC TSI 3025A as function of particle size has to be known, which is on the other hand dependent on sulfuric acid concentration. The DMPS measurements are done only for high concentrations of sulfuric acid; at low sulfuric acid concentrations we do not have sufficient particle number concentration to run DMPS, either $D_p = f(H_2SO_4)$.

Referee#1:

(v) Figure 10 is a nice picture that is presumably interpolated results from the PH-CPC. Firstly, the raw data should be shown: the particle numbers vs. radius at each axial position should be plotted in a separate plot. What is the sample flow rate for the PHCPC in these measurements? The difference in distributions on going from 8 to 12 SLpm flows is puzzling. (Firstly, what do the numbers in the legend mean? The same

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scale for each should be used.) Much higher numbers at the end of the reactor for the lower flow rate experiments is counterintuitive as less sulfuric will survive to this region compared to the higher flow conditions. Note also that these distributions are notably different than those presented by Ball et al. who also had natural convection concerns. Are the current temperature gradients larger than those of this earlier work?

Authors:

Yes, the interpolation is used in between measured (raw) values of total count to produce contour plot (figure 10). In new version of manuscript we will also present these data in form suggested by referee. The legend in figure 10 represents the total particle count. The same scale for both cannot be used without normalizing the total count, this will lead to loss of information: for higher resident time particles grow to higher sizes (above 1.5 nm) and are better detected with PH-CPC.

Inlet flow of PHCPC was 1.6 lpm. Condenser flow 0.3 lpm divided to ~ 0.06 lpm sample / 0.24 lpm Sheath. The saturator temperature of the UCPC (part of PHCPC) was increased from nominal 37 °C up to 43°C. Condenser temperature was kept at 10 °C that yields to the maximum saturation ratio of $S \approx 4.0$ (in default settings $S \approx 3.1$). This information will be also added to new version of the manuscript.

Our temperature gradient is comparable to Ball et al. (1999); it is $\sim 22^\circ\text{C}$ (from 47 °C in mixing unit to 25 °C at the wall of nucleation chamber). The mixing unit is still about five centimeters before the entrance to nucleation chamber, so the actual temperature gradient is even smaller. The temperature gradient in Ball et al. (1999) is $\sim 22 - 26^\circ\text{C}$ (from 44 - 48°C in mixing zone to 22 °C at the wall flow reactor).

Referee#1:

(vi) A measured WLF that is less than the very lowest it can be (fully developed laminar flow) raises concerns about the measurements of H₂SO₄. The authors should present their explanation for such low WLFs.

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Authors:

We agree that the WLF measurements do not agree with the calculated ones. We suspect this to be because of two reasons: 1.) The calculated WLF's are from a constant temperature where as we have a temperature gradient in the beginning of the tube, thus a different diffusion coefficient. 2.) The second reason is actually connected with the first one; the diffusion coefficient may be different than that suggested by Hanson and Eisele (2000). This is already so, as we are working with H₂SO₄ + air, where as the theoretical diffusion coefficient is of H₂SO₄ + N₂. The discussion on p. 23886 line 15 of the manuscript will be extended.

Referee#1:

(vii) There is additional concern that the J results for 30% RH are greater than the 50% RH results. This is not consistent with either theory or what has been published previously. Please comment.

Authors:

Yes, the data of RH 50% and 30% in J vs. [H₂SO₄] plot lie on top of each other. From the prediction of BHNT the data of RH 30% should lie about factor of 2 towards higher concentrations of sulfuric acid. Nevertheless we guess that the expected shift of factor of 2 is hidden in uncertainties connected with the bubbler experiment and not well known dependency of $D_p = f(\text{H}_2\text{SO}_4)$.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 23875, 2009.

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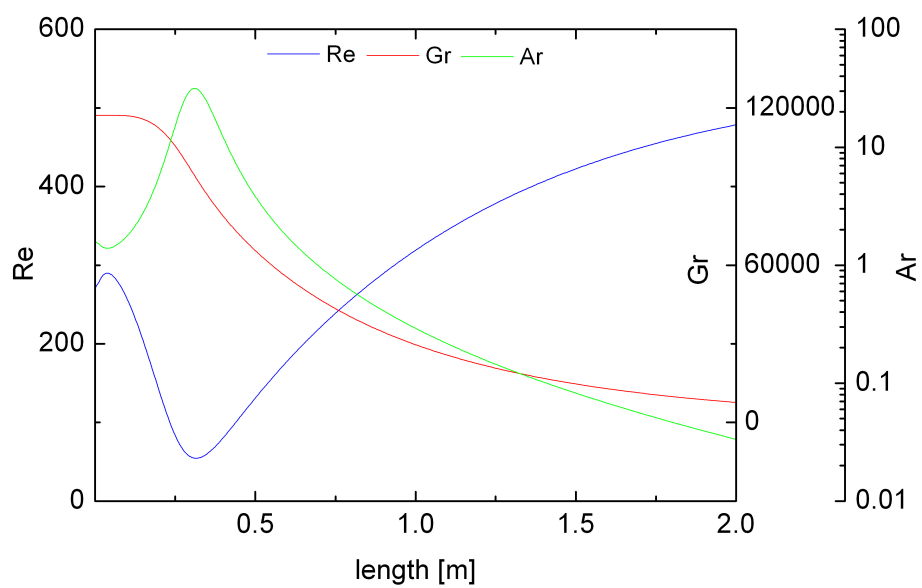


Fig. 1. Figure 1. Profiles of Reynolds, Grashof and Archimedes numbers at the axes as a function of distance in the nucleation chamber.