Atmos. Chem. Phys. Discuss., 14, C9701–C9704, 2014
www.atmos-chem-phys-discuss.net/14/C9701/2014/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "On the derivation of particle nucleation rates from experimental formation rates" *by* A. Kürten et al.

V.-M. Kerminen (Referee)

veli-matti.kerminen@helsinki.fi

Received and published: 28 November 2014

This manuscript presents an analysis on how nucleation rates should be derived from experimental particle formation rates, including those obtained from chamber experiments. Noting the increasingly important role of chamber experiments in studies of new-particle formation and growth, the topic of this paper is definitely a very important one.

The manuscript brings up an essential, yet not surprising, result: aerosol dynamics in an environmental chamber can be very different from that in the ambient atmosphere. Related to this, the authors 1) first demonstrate that the original method by KK2002 in deriving nucleation rates from measured particle formation rates is not applicable

to chamber experiments, and 2) then introduce a revised method which is generally applicable to such experiments. I very much welcome the point 2. I also think that it is valuable to discuss the limitations of earlier approaches (point 1), but such a discussion should be done in a correct way. I mainly agree with comments by the first anonymous reviewer. In addition to that, I have a few issues of my own for the authors to consider before recommending acceptance of this paper for publication.

The authors (K2014) spend two subsections (2.1 and 2.2 in K2014) to demonstrate why the KK2002 method does not perform well with typical chamber experiments. At the end of page 27236 (lines19-21) and also on page 2740 (lines 2-4), K2014 give readers the impression that the failure of KK2002 method in chamber experiments is due to some other reason than violation against the assumptions 1-3 (see line 10 on page 27236) which were stated very clearly in the original manuscript by KK2002. This is not correct. K2014 shows that in chamber experiments, the main sink for small nucleated clusters is either chamber walls or small (<10 nm) nuclei formed earlier during the experiment. A large chamber wall sink clearly violates the assumption 1, while a large sink by small nuclei violates either the assumption 1 or assumption 3 depending on how "pre-existing larger particles" are being defined (admittedly, this definition was a bit loose in KK2002). Most atmospheric aerosol scientists would not call 3-10 nm particles as "larger pre-existing particles", in which case the large sink by such particles would violate the assumption 1. K2014 tends to categorize these 3-10 nm particles as part of the sub-population of "larger pre-existing particles". In this interpretation, the large sink caused by such particles violates the assumptions 3, since this sub-population undergoes major changes during the experiment. In summary: KK2002 fails in chamber experiments because the conditions in such experiments violate the very clearly-stated assumptions in the original paper by KK2002. This is definitely a valuable point to bring up in K2014, even though essentially the same information is already available in KK2002. At least some revisions of the in subsection 2.1 and 2.2 are necessary based on the arguments above.

K2014 introduces a new method to derive nucleation rates from measured particle formation rates which works for chamber experiments. Very good, in principle! However, I am not confident that the new method can be called universal. The method takes into account the influence of self-coagulation on the nuclei number concentration (the term j=m in the r.h.s of Eq. 25), but does it take into account the influence of self-coagulation on the nuclei growth rate (Eq. 4)? The times scales over which nuclei self coagulation affects their number concentration and growth are so similar that these two processes become important under roughly the same conditions. Furthermore, is it possible that Jm in Eq. 4 is independent of the nuclei number concentration in the previous size bin (m-1)? One more related issue: the approach used in the new method is not entirely original either. Already K2004 (Aerosol Sci. Technol. 38, p. 1001-1008, equations 7 and 8 and the text) introduces the idea of adding extra bins below the size m shown in Fig. 3 by K2012, and then corrects the apparent particle formation rate when calculating toward the initial nucleation diameter. Of course, K2014 goes beyond K2004 in that K2004 does not take into account the effect of self-coagulation.

Other issues:

Since there are several pieces of work on the issue addressed in this work between K2014 and the original paper by K2002, and since most of the readers probably will not go through all the details in sections 2 and 3, I would recommend adding a brief review of the conducted work made after K2002 into the last paragraph of section 1.

In section 4, the authors should more explicitly bring up the limitations of the new method in determining the original nucleation rate. First, none of the methods developed so far, including the one introduced here, cannot reproduce a correct nucleation rate unless the size-dependent nuclei growth rate is known down to the size where the nucleation occurs (dnuc). This is a major problem because this information is almost never available and when it is, even small uncertainties in it cause large errors (see Figure 7 by K2014 as well as in earlier works on this topic). Second, we do not really know which value of dnuc to apply when estimating the nucleation rate. This definitely

affects the result as well. Third, does the new method really work when self-coagulation becomes important?

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 27233, 2014.