

**Influence of aerosol
lifetime – nucleation
experiments**

S. Ehrhart and J. Curtius

Influence of aerosol lifetime on the interpretation of nucleation experiments with respect to the first nucleation theorem

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

The SAWNUC microphysical aerosol nucleation model is used to study the effect of reactor walls on the interpretation of nucleation experiments with respect to nucleation theory. This work shows that loss processes, such as wall losses, influence the interpretation of nucleation experiments, especially at low growth rates and short lifetime of freshly nucleated particles. In these cases the power dependency of the formation rates, determined at a certain particle size, with respect to H_2SO_4 does not correspond to the approximate number of H_2SO_4 molecules in the critical cluster as expected by the first nucleation theorem. Observed $\partial \log(J)/\partial \log([\text{H}_2\text{SO}_4])$ therefore can vary widely for identical nucleation conditions but different sink terms.

1 Introduction

Nucleation of aerosol particles is a frequent phenomenon in the atmosphere (Kulmala et al., 2004). Losses of nucleating clusters and freshly formed particles to a population of pre-existing particles are common to proceed in parallel to the nucleation and early growth of the freshly formed particles. Similarly, in laboratory experiments losses to the wall of the reaction vessel and the dwell time in flow tubes limit the lifetime of the newly formed particles. These artifacts cannot be avoided. Raes and Janssens (1986) already used a detailed general dynamics model to correct their particle formation rates measured in chamber experiments. Kulmala et al. (2004) states that the “apparent” nucleation rate J_d at a given threshold diameter d , defined as the derivative of particle concentration with respect to time, equals the “true” nucleation rate J in systems without coagulation sinks. Here, “true” denotes the nucleation rate at the critical cluster size. Kerminen and Kulmala (2002) published an approach to take losses to pre-existing particles into account when correcting from measured formation rates to particle formation rates at a certain smaller diameter, usually a presumed critical diameter. Nevertheless, this approach does not include losses of clusters below the

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Influence of aerosol lifetime – nucleation experiments

S. Ehrhart and J. Curtius

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Influence of aerosol lifetime – nucleation experiments

S. Ehrhart and J. Curtius

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

critical size nor does it include losses to vessel walls or the limited dwell time in flow tubes. For laboratory measurements losses to walls of large chambers are usually assumed to be comparable to losses to pre-existing particles in ambient measurements (e.g. Kirkby et al., 2011), meaning the walls fulfil the same role as a population of large aerosol particles. As will be shown here, these sinks can influence the interpretation of nucleation measurements with respect to the first nucleation theorem.

Gas phase sulphuric acid (H_2SO_4) is considered to be the most important component in atmospheric aerosol nucleation (Weber et al., 1999; Curtius et al., 2006). The focus of this work is on the role of H_2SO_4 but the results are generally applicable to situations of aerosol nucleation with competing losses to walls or pre-existing particles. The first nucleation theorem states that the slope of $\log(J)$ as function of $\log([\text{H}_2\text{SO}_4])$ gives approximately the number of H_2SO_4 molecules, n^* , in the critical cluster (Kashchiev, 1982; Oxtoby and Kashchiev, 1994). n^* plays an important role for the microphysical interpretation of nucleation rate measurements. Currently different experiments on binary nucleation yield widely varying numbers for n^* in the range from 2 to 20, see for example Wyslouzil et al. (1991), Viisanen et al. (1997), Ball et al. (1999), Sipilä et al. (2010), Kirkby et al. (2011) and Zollner et al. (2012). Zollner et al. summarise the results in an overview table. One reason for these discrepancies can be the presence of contaminant vapours that cause ternary or multi-component nucleation and lower the free energy barrier for nucleation and therefore lead to a smaller observed n^* . The significant influence of ammonia on nucleation rates was, for example, shown in Ball et al. (1999) and Kirkby et al. (2011).

In nucleation experiments two different design concepts are commonly used: flow tube and chamber. The biggest difference between both designs is that chambers usually have longer dwell times than flow tubes. The gas in a chamber can be stirred, in a flow tube it is usually in a laminar flow. The dominant loss effect for particles and H_2SO_4 in case of the flow tube is the flow out of the reactor, resulting in an immediate stop of the nucleation and growth processes. In chamber experiments lifetimes of

H₂SO₄ are typically determined by diffusion to the wall and are usually on the order of several minutes.

In the present paper the SAWNUC model, Sulphuric Acid Water NUCleation (Lovejoy et al., 2004), is used to determine the n^* from simulated particle formation rates for different sizes of particles under conditions with and without wall losses present. SAWNUC is a microphysical model that describes binary aerosol nucleation and growth for neutral and ion-induced nucleation pathways of the sulphuric acid/water system.

This work shows that for situations where loss rates become comparable to cluster growth rates (molecules s⁻¹), the slopes of the logarithm of apparent nucleation rate, $\log(J_d)$, as a function of $\log([H_2SO_4])$ do not yield the approximate number of H₂SO₄ molecules in the critical cluster anymore. These losses can yield values of n^* from the apparent nucleation rate that are much higher than the “true” n^* . This situation applies for many atmospheric measurements of nucleation as well as for laboratory studies of nucleation intending to simulate atmospheric conditions (i.e. $[H_2SO_4] < 1 \cdot 10^7 \text{ cm}^{-3}$ and H₂SO₄ sinks $> 0.001 \text{ s}^{-1}$, Kulmala et al., 2005).

When a significant sink is present the nucleation rate has to be determined at the critical diameter to yield correct values of n^* . A correction from an apparent nucleation rate to the “true” nucleation rate can be impeded as the critical size is not a priori known.

2 Methods

The SAWNUC model was used to calculate the steady state formation rate of particles exceeding a certain diameter at constant H₂SO₄ concentration, relative humidity and temperature. The calculation included particles up to a diameter of 3.5 nm. A particle containing i sulphuric acid molecules can undergo several processes that change the concentration $[i]$ of that particular species of particles. For a detailed description of processes and their rate constants see Lovejoy et al. (2004) and Kazil and Lovejoy (2007). Several processes change the concentration of i -clusters. Besides condensation and

Influence of aerosol lifetime – nucleation experiments

S. Ehrhart and J. Curtius

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



evaporation of H_2SO_4 molecules these include coagulation with other charged or uncharged clusters, as well as coagulation with a fixed population of pre-existing aerosol particles and losses to reactor walls. To simulate conditions of a laboratory experiment of nucleation, the following loss term to simulate chamber walls was added to the equations of Lovejoy et al. (2004):

$$L_i^w = -k_i^w [i]. \quad (1)$$

Here k_i^w is described by,

$$k_i^w = C \sqrt{D_i}, \quad (2)$$

an approach already described in Metzger et al. (2010). The diffusion coefficient D_i is a function of particle diameter and temperature and calculated by the Millikan-Cunningham corrected Stokes-Einstein diffusion (Baron and Willeke, 2001). The factor C is chosen to produce the lifetime of H_2SO_4 . Note that the diffusion coefficient of Hanson and Eisele (2000) for H_2SO_4 was not used in this calculation. The diffusion coefficient of sulphuric acid was calculated the same way as for particles, yielding a diffusion coefficient of $0.13 \text{ cm}^2 \text{ s}^{-1}$, in order to have a consistent description of the size dependence rather than a consistent description of temperature dependence of H_2SO_4 diffusion.

It should be noted that losses to pre-existing particles or vessel walls are not equivalent to evaporation of sub critical clusters. The condensational sink effectively removes clusters and particles from the system and thus is not contributing to the equilibrium before the critical cluster. This violates one of the most important assumptions of the nucleation theorem, the thermodynamic equilibrium of subcritical clusters.

For particle formation rates, J_d , at different mass diameters d the number of H_2SO_4 molecules in the “apparent” critical cluster n_d^* was calculated from,

$$n_d^* = \frac{\partial \log(J_d)}{\partial \log([\text{H}_2\text{SO}_4])}. \quad (3)$$

Influence of aerosol lifetime – nucleation experiments

S. Ehrhart and J. Curtius

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

The particle formation rate represents the net flux of particles exceeding the diameter d towards bigger diameters. It is therefore equivalent to a formation rate as it would be measured by a particle counter with a step function counting efficiency that starts counting at d nm. If no additional losses occur, $n_d^* \approx n^*$.

A kinetic approach to determine the critical cluster is described by Kazil and Lovejoy (2007). In case of this method it is assumed that the critical cluster is the smallest cluster for which,

$$k_i^a[\text{H}_2\text{SO}_4] \geq k_i^e, \quad (4)$$

is fulfilled. Here k_i^e is the rate constant of evaporation and k_i^a is the rate constant of sulphuric acid uptake. This approach is only valid for nucleation that is limited by a single free energy barrier.

In case of additional losses (or source terms) the condition for a cluster where growth exceeds losses must be written as,

$$k_i^a[\text{H}_2\text{SO}_4] + q_i^c \geq k_i^e + L_i^c + L_i^w. \quad (5)$$

On the left hand side an additional source term was introduced that represents production of particles due to coagulation. On the right hand side L_i^c represents losses due to coagulation while L_i^w is the wall loss term described above. Under most conditions, $q_i^c \ll L_i^c + L_i^w$, this effectively increases the size of the “apparent” critical cluster.

Simulations were done at different conditions. The temperature was set to 248 K. At this temperature the effects of neutral and ion-induced nucleation (IIN) overlap already at intermediate H_2SO_4 concentrations. The ion pair production rate was set to 0 or 5 ion pairs $\text{cm}^{-3} \text{s}^{-1}$, thus providing insight in the influence of ion-induced nucleation on the determination of n_d^* and hence n^* . The lifetime of H_2SO_4 with respect to the walls, i.e. $(k_{\text{H}_2\text{SO}_4}^w)^{-1}$, was varied to represent different laboratory conditions. Due to similarity between wall loss and condensation sink, the results can also be transferred to atmospheric conditions. Furthermore two different free energy surfaces were applied.

Influence of aerosol lifetime – nucleation experiments

S. Ehrhart and J. Curtius

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



In one case the original free energies (Lovejoy and Curtius, 2001; Curtius et al., 2001; Lovejoy et al., 2004) were used to determine the evaporation of particles, in another case, no evaporation was assumed thus giving nucleation in the kinetic limit.

3 Results

Simulation results of n_d^* derived from the sensitivity of $\log(J_d)$ to $\log(\text{H}_2\text{SO}_4)$ for 248 K with a H_2SO_4 lifetime of 500 s are shown in Fig. 1. The black line connects the integer numbers of H_2SO_4 molecules in the neutral critical cluster derived from Eq. (4), the blue line labelled J_{crit} shows n^* derived from the slope of the logarithm of the “true” nucleation rate. The red lines labelled J_d show n_d^* derived from formation rates of particles with mass diameter exceeding d nm. The green solid line shows the “true” nucleation rate while the dashed green line shows the formation rate of particles with a diameter of 1.7 nm. Both rates lie close each other and for low concentrations of H_2SO_4 the value is too low to be measured. In this system the effect of walls or condensational sinks has therefore only minor influence on the interpretation of nucleation experiments in terms of the first nucleation theorem. In case of a particle counter that measures sub-critical clusters, here shown for a case of 1 nm, the derived $n_{1.0}^*$ is independent of the H_2SO_4 concentration but is below the “true” n^* over a wide range of $[\text{H}_2\text{SO}_4]$.

Vehkamäki et al. (2012) studied the effect of stable clusters smaller than the critical diameter on the interpretation of the nucleation theorem. This situation is given in the case of ion-induced nucleation. SAWNUC contains measured evaporation rates for negatively charged clusters, (Curtius et al., 2001; Froyd and Lovejoy, 2003) and can therefore be used to study the effect of charged clusters on the nucleation theorem. The important feature of charged nucleation is that it provides a faster route to stable aerosols. This is achieved by a lower rate of evaporation and an enhanced rate of condensation due to charge dipole interactions of the charged cluster and the condensing H_2SO_4 (Su and Chesnavich, 1982; Yu and Turco, 1998). After reaching a stable size, recombination with ions of opposite polarity yields stable neutral particles. The results

Influence of aerosol lifetime – nucleation experiments

S. Ehrhart and J. Curtius

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Influence of aerosol lifetime – nucleation experiments

S. Ehrhart and J. Curtius

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



of a simulation with an ion pair production rate of $5 \text{ ion pairs cm}^{-3} \text{ s}^{-1}$ are shown in Fig. 2. The black line corresponds to the amount of H_2SO_4 in the critical cluster based on neutral thermodynamics (Eq. 4). For most of the simulated particle formation rates, n^* falls below the theoretically expected value for neutral nucleation at a certain H_2SO_4 concentration. For very high concentrations of H_2SO_4 the neutral line based on Eq. (4) and the lines derived from J_i fall together. In these cases the neutral nucleation channel dominates and the contribution from the charged channel becomes insignificant. This effect can also be seen from the nucleation rate respectively the particle formation rate (green curves in Fig. 2). J_{crit} and $J_{1.7}$ are at low concentration of H_2SO_4 mainly driven by ion-induced nucleation, the effect of ions decreases at $[\text{H}_2\text{SO}_4] \approx 1 \cdot 10^7 \text{ cm}^{-3}$ and in case of insignificant neutral contribution, it would reach eventually the value of the ion pair production rate, see also Raes et al. (1986). In this example the neutral nucleation starts to contribute to the total nucleation rate in the region of $[\text{H}_2\text{SO}_4]$ between $1 \cdot 10^7$ and $1 \cdot 10^8 \text{ cm}^{-3}$ and eventually becomes the main source of particle formation. For a particle counter with a threshold diameter 1 nm, $n_{1.0}^*$ lies below the actual n^* for $[\text{H}_2\text{SO}_4] < 1 \cdot 10^7 \text{ cm}^{-3}$. This changes when the critical diameter for the charged channel becomes smaller with higher $[\text{H}_2\text{SO}_4]$.

Recent research implies that nucleation under atmospheric conditions can proceed at or close to the kinetic limit, especially in case of ternary nucleation (Metzger et al., 2010; Paasonen et al., 2012). Therefore the energy barrier in neutral nucleation was removed in SAWNUC and simulations under neutral conditions and varying concentrations of H_2SO_4 were performed. The lifetime of H_2SO_4 due to walls was set to 500 s as before. This gives a reasonable approximation processes in ternary systems with sulphuric acid being the vapour with the lowest concentration and therefore being the limiting species for growth and nucleation of particles. From Fig. 3 it can be seen that also in such a system strong deviations between the “true” n^* and the “apparent” n_d^* exist. These are also caused by the losses of the nucleating and growing clusters to walls or, in case of atmospheric measurements, pre-existing particles. As in previous plots the green curves show formation rates. While J_{crit} follows a straight line with a slope

of two as expected, $J_{1.7}$ shows a strong curvature depending on the concentration of H_2SO_4 . Even in the case of the same slope $J_{1.7}$ does not reach the same value as J_{crit} due to self-coagulation of nucleating particles. Self-coagulation of nucleating particles was allowed in order to have a realistic description of nucleation in a clean experimental environment.

Simulation results for n_d^* as function of the wall loss lifetime of H_2SO_4 , for 248 K and $[\text{H}_2\text{SO}_4]=2.3 \cdot 10^6 \text{ cm}^{-3}$, are shown in Fig. 4. Labels are the same as in the previous figure and calculations were performed with evaporation rates removed. In case of a wall loss and an environment free of pre-existing particles, n_d^* from all formation rates basically match each other and $n_d^* = n^*$, for all d . The deviation in n^* between the different cut-offs increases linearly with increasing particle losses, with steeper increases for higher cut-offs. The comparison between the “true” nucleation rate, J_{crit} green solid curve, and the formation rate of particles exceeding 1.7 nm, $J_{1.7}$ green dashed curve, shows a big influence of wall losses. As mentioned above, both green lines do not merge at $k^w = 0$ due to self-coagulation of the nucleating particles. $J_{1.7}$ shows a strong dependency on the wall loss rate and can suppress nucleation significantly, thus acting similar to an energy barrier and decreasing the particle formation rate significantly.

4 Conclusions

In this work it was shown that losses of small particles have to be taken into account when interpreting the slopes of a $\log(J_d)$ vs $\log([\text{H}_2\text{SO}_4])$ plot. In laboratory experiments, flow tube or chamber, nucleating particles will be lost to the walls or removed from the vessel, in atmospheric measurements these particles will be lost to pre-existing larger aerosols. But these sinks differ from reactor to reactor and in the atmosphere pre-existing aerosol concentration and size distribution differ with time and location. Comparing results from different experiments can therefore lead to a bias in the interpretation of the experiment when these are interpreted in terms of the first nucleation theorem. This is especially valid when the “true” size of the critical cluster

Influence of aerosol lifetime – nucleation experiments

S. Ehrhart and J. Curtius

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Influence of aerosol lifetime – nucleation experiments

S. Ehrhart and J. Curtius

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



is not a priori known and the interpretation has to be based on formation rates of particles exceeding a certain diameter. This bias can only be avoided when the growth rates are high enough so that the characteristic time of growing the particles is much smaller than the lifetime of the particles determined by the sink. Correcting measured formation rates to an assumed critical size can reduce this error but assuming a critical size introduces another bias.

The situation becomes more complex in cases where another route to stable particles exists, for example ion-induced nucleation. Ternary nucleation that competes with binary nucleation is another factor that needs to be taken into account. And in even more complex cases ternary nucleation could proceed through different channels, depending on the availability and nature of condensable vapours. Here it was shown that even in the most simple case of nucleation that is not limited by formation of a critical cluster interpreting the measurements in terms of the first nucleation theorem can give spurious results.

The introduction of a sink is mathematically similar to introducing a small but significant evaporation term to all clusters, although the microphysical difference between both processes remains. Therefore the results presented for this case can also be applied to nucleation without energy barrier but with some evaporation. The condensational sink can also be seen as equivalent to a limited dwell time in a reactor. Especially flow tube reactors have typically short dwell times (e.g. Ball et al., 1999; Young et al., 2008; Zollner et al., 2012) and are therefore similar to systems with high condensational sinks.

Our overall conclusion is that the measured power dependency of nucleation rates on H_2SO_4 cannot be directly interpreted in terms of the number of H_2SO_4 molecules in the critical cluster, as suggested by the first nucleation theorem. It is therefore more appropriate to interpret the thermodynamics of such systems with microphysical models such as SAWNUC. A model describing nucleation from the growing monomer has the advantage of taking processes into account which are usually ignored in classical

nucleation theory. Non-equilibrium processes, such as losses to pre-existing particles or walls, that occur to clusters smaller than the critical cluster need to be included.

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References

- Ball, S. M., Hanson, D. R., Eisele, F. L., and McMurry, P. H.: Laboratory studies of particle nucleation: initial results for H_2SO_4 , H_2O , and NH_3 vapors, *J. Geophys. Res.*, 104, 23709–23718, doi:10.1029/1999JD900411, 1999. 9735, 9742
- Baron, P. A. and Willeke, K.: *Aerosol Measurement*, Wiley Interscience, United States of America, 2 edn., New York, 2001. 9737
- Curtius, J., Froyd, K. D., and Lovejoy, E. R.: Cluster ion thermal decomposition (I): experimental kinetics study and ab initio calculations for $\text{HSO}_4^- (\text{H}_2\text{SO}_4)_x (\text{HNO}_3)_y$, *J. Phys. Chem. A*, 105, 10867–10873, doi:10.1021/jp0124950, 2001. 9739
- Curtius, J., Lovejoy, E., and Froyd, K.: Atmospheric ion-induced aerosol nucleation, *Space Sci. Rev.*, 125, 159–167, doi:10.1007/s11214-006-9054-5, 2006. 9735
- Froyd, K. D. and Lovejoy, E. R.: Experimental thermodynamics of cluster ions composed of H_2SO_4 and H_2O , 2: measurements and ab initio structures of negative ions, *J. Phys. Chem. A*, 107, 9812–9824, doi:10.1021/jp0278059, 2003. 9739
- Hanson, D. R. and Eisele, F.: Diffusion of H_2SO_4 in humidified nitrogen: hydrated H_2SO_4 , *J. Phys. Chem. A*, 104, 1715–1719, doi:10.1021/jp993622j, 2000. 9737
- Kashchiev, D.: On the relation between nucleation work, nucleus size, and nucleation rate, *J. Chem. Phys.*, 76, 5098–5102, doi:10.1063/1.442808, 1982. 9735
- Kazil, J. and Lovejoy, E. R.: A semi-analytical method for calculating rates of new sulfate aerosol formation from the gas phase, *Atmos. Chem. Phys.*, 7, 3447–3459, doi:10.5194/acp-7-3447-2007, 2007. 9736, 9738
- Kerminen, V.-M. and Kulmala, M.: Analytical formulae connecting the “real” and the “apparent” nucleation rate and the nuclei number concentration for atmospheric nucleation events, *J. Aerosol Sci.*, 33, 609–622, doi:10.1016/S0021-8502(01)00194-X, 2002. 9734

Influence of aerosol lifetime – nucleation experiments

S. Ehrhart and J. Curtius

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Influence of aerosol lifetime – nucleation experiments

S. Ehrhart and J. Curtius

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- Kirkby, J., Curtius, J., Almeida, J., Dunne, E., Duplissy, J., Ehrhart, S., Franchin, A., Gagne, S., Ickes, L., Kürten, A., Kupc, A., Metzger, A., Riccobono, F., Rondo, L., Schobesberger, S., Tsagkogeorgas, G., Wimmer, D., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Downard, A., Ehn, M., Flagan, R. C., Haider, S., Hansel, A., Hauser, D., Jud, W., Junninen, H., Kreissl, F., Kvashin, A., Laaksonen, A., Lehtipalo, K., Lima, J., Lovejoy, E. R., Makhmutov, V., Mathot, S., Mikkilä, J., Minginette, P., Mogo, S., Nieminen, T., Onnela, A., Pereira, P., Petäjä, T., Schnitzhofer, R., Seinfeld, J. H., Sipilä, M., Stozhkov, Y., Stratmann, F., Tomé, A., Vanhanen, J., Viisanen, Y., Vrtala, A., Wagner, P. E., Walther, H., Weingartner, E., Wex, H., Winkler, P. M., Carslaw, K. S., Worsnop, D. R., Baltensperger, U., and Kulmala, M.: Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation, *Nature*, 476, 429–433, 2011. 9735
- Kulmala, M., Vehkamäki, H., Petäjä, T., Maso, M. D., Lauri, A., Kerminen, V.-M., Birmili, W., and McMurry, P.: Formation and growth rates of ultrafine atmospheric particles: a review of observations, *J. Aerosol Sci.*, 35, 143–176, doi:10.1016/j.jaerosci.2003.10.003, 2004. 9734
- Kulmala, M., Petäjä, T., Mönkkönen, P., Koponen, I. K., Dal Maso, M., Aalto, P. P., Lehtinen, K. E. J., and Kerminen, V.-M.: On the growth of nucleation mode particles: source rates of condensable vapor in polluted and clean environments, *Atmos. Chem. Phys.*, 5, 409–416, doi:10.5194/acp-5-409-2005, 2005. 9736
- Lovejoy, E. R. and Curtius, J.: Cluster ion thermal decomposition (II): master equation modeling in the low-pressure limit and fall-off regions, bond energies for $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_x(\text{HNO}_3)_y$, *J. Phys. Chem. A*, 105, 10874–10883, doi:10.1021/jp012496s, 2001. 9739
- Lovejoy, E. R., Curtius, J., and Froyd, K. D.: Atmospheric ion-induced nucleation of sulfuric acid and water, *J. Geophys. Res.-Atmos.*, 109, D08204, doi:10.1029/2003JD004460 2004. 9736, 9737, 9739
- Metzger, A., Verheggen, B., Dommen, J., Duplissy, J., Prevot, A. S. H., Weingartner, E., Riipinen, I., Kulmala, M., Spracklen, D. V., Carslaw, K. S., and Baltensperger, U.: Evidence for the role of organics in aerosol particle formation under atmospheric conditions, *P. Natl. Acad. Sci. USA*, 107, 6646–6651, 2010. 9737, 9740
- Oxtoby, D. W. and Kashchiev, D.: A general relation between the nucleation work and the size of the nucleus in multicomponent nucleation, *J. Chem. Phys.*, 100, 7665–7671, doi:10.1063/1.466859, 1994. 9735
- Paasonen, P., Olenius, T., Kupiainen, O., Kurtén, T., Petäjä, T., Birmili, W., Hamed, A., Hu, M., Huey, L. G., Plass-Duelmer, C., Smith, J. N., Wiedensohler, A., Loukonen, V., McGrath, M. J.,

Influence of aerosol lifetime – nucleation experiments

S. Ehrhart and J. Curtius

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Ortega, I. K., Laaksonen, A., Vehkamäki, H., Kerminen, V.-M., and Kulmala, M.: On the formation of sulphuric acid – amine clusters in varying atmospheric conditions and its influence on atmospheric new particle formation, *Atmos. Chem. Phys.*, 12, 9113–9133, doi:10.5194/acp-12-9113-2012, 2012. 9740

5 Raes, F. and Janssens, A.: Ion-induced aerosol formation in a H_2O - H_2SO_4 system – II: numerical calculations and conclusions, *J. Aerosol Sci.*, 17, 715–722, doi:10.1016/0021-8502(86)90051-0, 1986. 9734

Raes, F., Janssens, A., and Dingenen, R. V.: The role of ion-induced aerosol formation in the lower atmosphere, *J. Aerosol Sci.*, 17, 466–470, doi:10.1016/0021-8502(86)90135-7, 1986. 9740

10 Sipilä, M., Berndt, T., Petäjä, T., Brus, D., Vanhanen, J., Stratmann, F., Patokoski, J., Mauldin III, R. L., Hyvärinen, A.-P., Lihavainen, H., and Kulmala, M.: The role of sulfuric acid in atmospheric nucleation, *Science*, 327, 1243–1246, 2010. 9735

Su, T. and Chesnavich, W. J.: Parametrization of the ion–polar molecule collision rate constant by trajectory calculations, *J. Chem. Phys.*, 76, 5183–5185, doi:10.1063/1.442828, 1982. 9739

Vehkamäki, H., McGrath, M. J., Kurtén, T., Julin, J., Lehtinen, K. E. J., and Kulmala, M.: Rethinking the application of the first nucleation theorem to particle formation, *J. Chem. Phys.*, 136, 094107, doi:10.1063/1.3689227, 2012. 9739

20 Viisanen, Y., Kulmala, M., and Laaksonen, A.: Experiments on gas–liquid nucleation of sulfuric acid and water, *J. Chem. Phys.*, 107, 920–926, doi:10.1063/1.474445, 1997. 9735

Weber, R. J., McMurry, P. H., Mauldin, R. L., Tanner, D. J., Eisele, F. L., Clarke, A. D., and Kapustin, V. N.: New particle formation in the remote troposphere: a comparison of observations at various sites, *Geophys. Res. Lett.*, 26, 307–310, doi:10.1029/1998GL900308, 1999. 9735

25 Wyslouzil, B. E., Seinfeld, J. H., Flagan, R. C., and Okuyama, K.: Binary nucleation in acid–water systems, II: sulfuric acid–water and a comparison with methanesulfonic acid–water, *J. Chem. Phys.*, 94, 6842–6850, doi:10.1063/1.460262, 1991. 9735

30 Young, L. H., Benson, D. R., Kameel, F. R., Pierce, J. R., Junninen, H., Kulmala, M., and Lee, S.-H.: Laboratory studies of $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ binary homogeneous nucleation from the $\text{SO}_2 + \text{OH}$ reaction: evaluation of the experimental setup and preliminary results, *Atmos. Chem. Phys.*, 8, 4997–5016, doi:10.5194/acp-8-4997-2008, 2008. 9742

Yu, F. and Turco, R. P.: The formation and evolution of aerosols in stratospheric aircraft plumes: numerical simulations and comparisons with observations, *J. Geophys. Res.*, 103, 25915–25934, 1998. 9739

5 Zollner, J. H., Glasoe, W. A., Panta, B., Carlson, K. K., McMurry, P. H., and Hanson, D. R.: Sulfuric acid nucleation: power dependencies, variation with relative humidity, and effect of bases, *Atmos. Chem. Phys.*, 12, 4399–4411, doi:10.5194/acp-12-4399-2012, 2012. 9735, 9742

Influence of aerosol lifetime – nucleation experiments

S. Ehrhart and J. Curtius

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Influence of aerosol lifetime – nucleation experiments

S. Ehrhart and J. Curtius

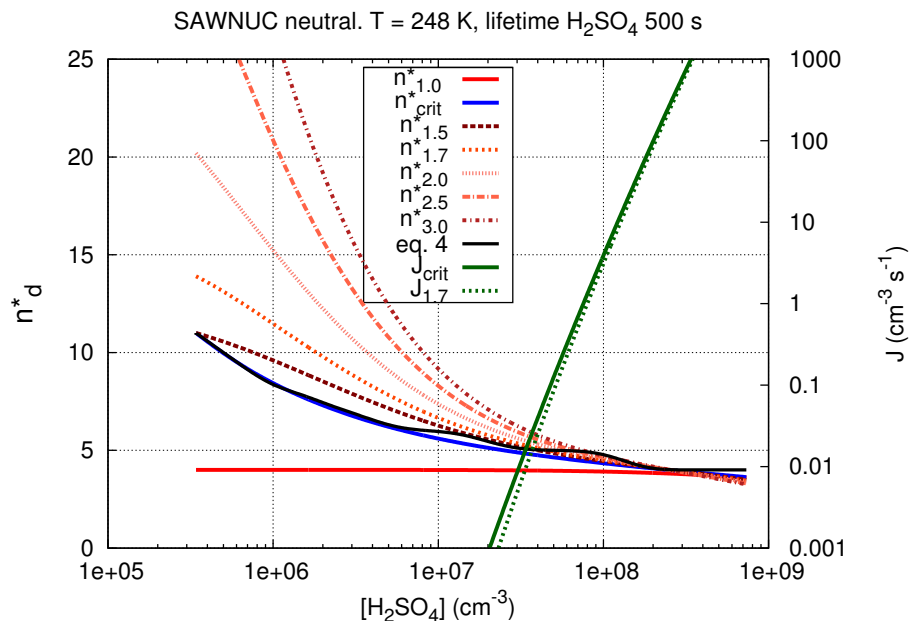


Fig. 1. Examples of the influence of different cut-off diameters on the interpretation of measurements of neutral particle formation rates at $T = 248$ K and H_2SO_4 lifetime of 500 s. Red lines show n^*_d and the blue lines n^* derived from Eq. (3). The black line shows n^* from Eq. (4). The solid green line shows the “true” nucleation rate, while the dashed green line shows the formation rate of particles exceeding 1.7 nm, i.e. the apparent nucleation rate. Values for both green lines can be taken from the right axis.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Influence of aerosol lifetime – nucleation experiments

S. Ehrhart and J. Curtius

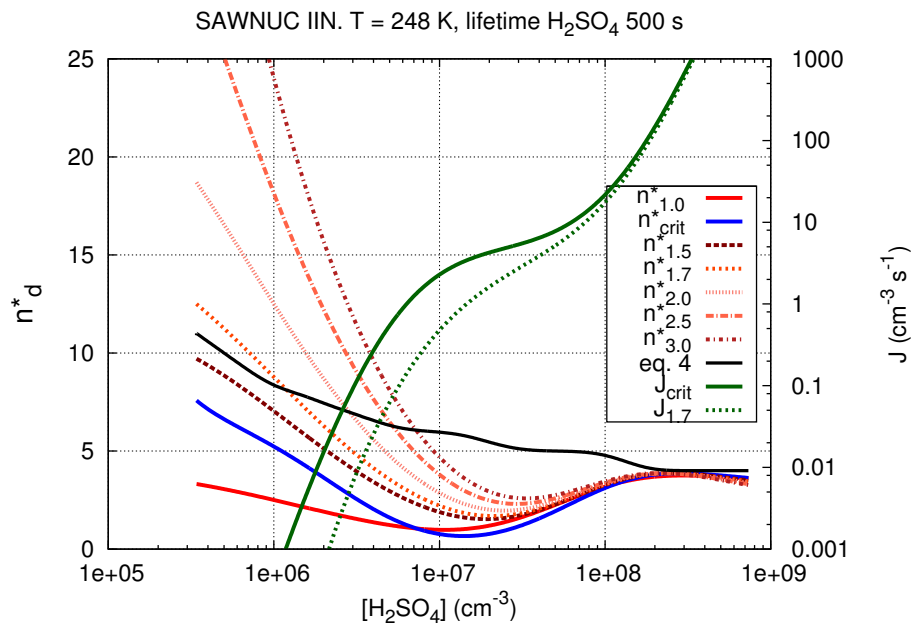


Fig. 2. Influence of an ion-induced nucleation channel and a sink for small particles on the interpretation of measurements of particle formation rates. The minimum in n^* is around $1 \cdot 10^7 \text{ cm}^{-3}$ at 1.3. The labels and axis are the same as in Fig. 1.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Influence of aerosol lifetime – nucleation experiments

S. Ehrhart and J. Curtius

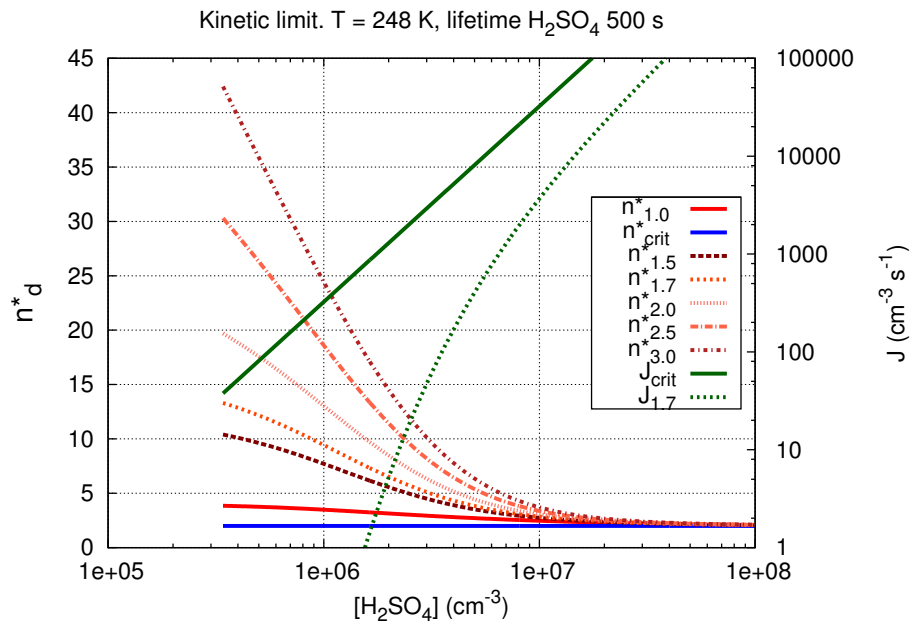


Fig. 3. Influence of a sink on the interpretation of measurements of particle formation rates in case of kinetically limited nucleation. In such a system strong deviations between the “true” n^* (blue line) and the “apparent” n_d^* (red lines) exist for the entire range of atmospherically-relevant H_2SO_4 concentrations and nucleation rates. The labels and axis are the same as in Fig. 1.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Influence of aerosol lifetime – nucleation experiments

S. Ehrhart and J. Curtius

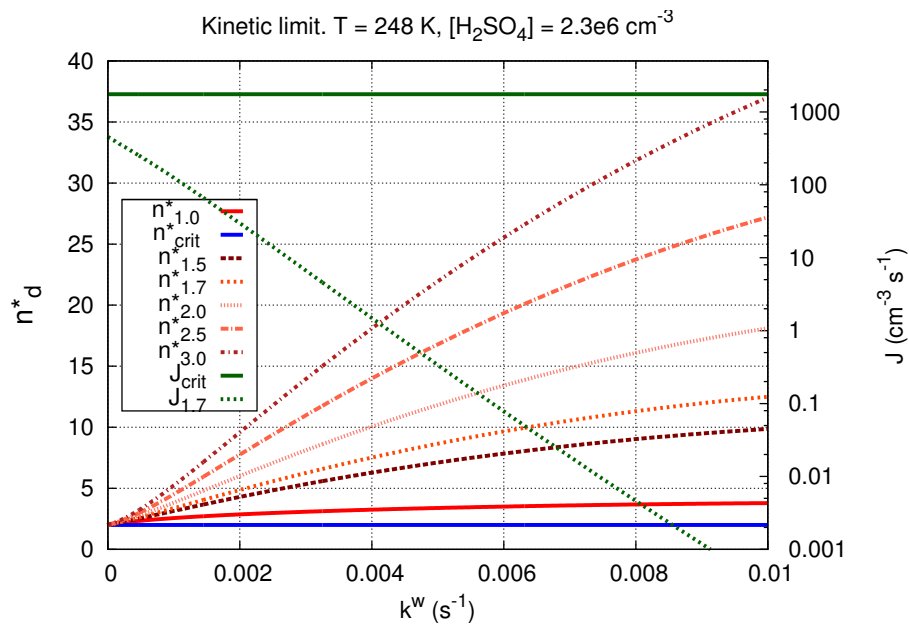


Fig. 4. n_d^* vs. wall loss rate coefficient k^w for $[\text{H}_2\text{SO}_4]=2.3 \cdot 10^6 \text{ cm}^{-3}$ and no evaporation of nucleating particles. Labels are the same as in Fig. 1.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

