New parameterization of sulfuric acid-ammonia-water ternary nucleation rates at tropospheric conditions

J. Merikanto,[1] I. Napari,[1] H. Vehkamäki,[1] T. Anttila,[2] and M. Kulmala[1]

[1]   Recently, the classical theory of sulfuric acid-ammonia-water (H_2SO_4-NH_3-H_2O) nucleation was reinvestigated by including the effect of stable ammonium bisulfate formation into calculations. The predicted nucleation rates lowered by many orders of magnitude, bringing them close to agreement with the available experiments on H_2SO_4-NH_3-H_2O nucleation. However, because of complex thermodynamics involved, the theoretical calculations of nucleation rates are computationally demanding, and sometimes the theory breaks down at specific concentrations and temperatures. Here we present parameterized equations of ternary H_2SO_4-NH_3-H_2O nucleation rates, critical cluster sizes, and critical cluster compositions. Our parameterizations reduce the computing time of these values by a factor of 10^5 compared with the calculations with the full thermodynamic model. Also, our parameterizations provide reliable estimates for ternary nucleation rates in cases when the full theory fails in isolated points of the parameter space. The parameterized nucleation rates are accurate to one order of magnitude in nucleation rate. Because of their computational efficiency, our parameterizations are particularly suitable for large-scale models of atmosphere. They are valid for temperatures above 235 K, sulfuric acid concentrations $5 \cdot 10^4$–10^9 cm^{-3}, ammonia mixing ratios 0.1–1000 ppt, relative humidities 5%–95%, and nucleation rates over 10^{-5} cm^{-3} s^{-1}. At these conditions, no significant nucleation occurs above 295 K.

1.   Introduction

[2]   Current thinking in atmospheric sciences considers homogeneous nucleation of water and certain trace gases responsible for new particle formation in the atmosphere [*Kulmala et al.*, 2004b]. Since 1960s, it has been obvious that even small amounts of sulfuric acid cause a tremendous increase in nucleation rates of water in laboratory conditions [*Doyle*, 1961], and later simultaneous measurements of particle production and vapor composition in the atmosphere have shown that sulfuric acid concentration is indeed strongly correlated with particle formation rates [*Weber et al.*, 1996; *Kulmala et al.*, 2004a]. Sulfuric acid alone, however, is not always able to explain the high number of particles produced, for example, in marine [*Covert et al.*, 1992; *Hoppel et al.*, 1994] and coastal [*O'Dowd et al.*, 1999] boundary layer and in boreal forests [*Mäkelä et al.*, 1997], and one is forced to contemplate resorting to more complicated nucleation schemes or other formation mechanisms.

[3]   Ammonia is a ubiquitous substance in the atmosphere with the known ability to lower partial pressure of sulfuric acid above the solution surface [*Scott and Cattell*, 1979].

With this knowledge, involvement of ammonia in atmospheric nucleation was suggested [*Scott and Cattell*, 1979; *Coffman and Hegg*, 1995], and subsequent theoretical calculations [*Korhonen et al.*, 1999; *Napari et al.*, 2002a] showed that the ternary H_2SO_4-NH_3-H_2O nucleation rates exceeded binary H_2SO_4-H_2O nucleation rates by many orders of magnitude. The laboratory experiments [*Ball et al.*, 1999] also indicated an enhancement in the nucleation rates with the presence of ammonia, although to a lesser extent than predicted by the theoretical calculations; the experimental ternary nucleation rates exceeded the binary nucleation rates by only about two orders of magnitude. Comparisons with experimental field measurement data showed that the nucleation rates obtained from the theoretical model were too high; in fact, the model predicted nucleation happening all the time. A similar conclusion was reached by *Lucas and Akimoto* [2006], who implemented the ternary nucleation scheme in a global atmospheric model and found that the theory predicts unrealistically high nucleation rates throughout the troposphere. Therefore other nucleation mechanisms, such as ion-induced nucleation [*Yu and Turco*, 2000; *Lee et al.*, 2003; *Laakso et al.*, 2004; *Lovejoy et al.*, 2004; *Eisele et al.*, 2006; *Iida et al.*, 2006; *Yu*, 2006a], participation of sulfuric acid in kinetic nucleation and activation mechanism [*Kulmala et al.*, 2006], and participation of organics in the nucleation process instead of ammonia [*Kavouras et al.*, 1999; *Kavouras and Stephanou*, 2002], became viable alternatives. It was also

[1]Department of Physical Sciences, University of Helsinki, Finland.
[2]Finnish Meteorological Institute, Helsinki, Finland.

speculated that, instead of cluster formation, the early growth to observable sizes might be the limiting step in the atmosphere. Regarding new particle formation in coastal areas, the recent research indicates that the phenomenon can be explained by nucleation and condensation of certain iodine oxides [*O'Dowd et al.*, 2002; *Burkholder et al.*, 2004]. Overall, it seems likely that different nucleation mechanisms act depending on the location and chemical species present in the atmosphere. However, the H_2SO_4-NH_3-H_2O nucleation is still a strong option for one of the key mechanisms, and more so, when it was realized that the bulk of the sulfuric acid in the atmosphere may be bound to ammonia molecules [*Vehkamäki et al.*, 2004].

[4] It is a well-known fact that, in vapor phase, water and sulfuric acid form hydrates, which are agglomerates containing one acid molecule and one or more water molecules. Formation of a critical cluster, more likely to grow than to decay, out of hydrates requires more energy than its formation from free molecules. Consequently, if part of the acid molecules is bound to hydrates, lower nucleation rates are obtained. *Korhonen et al.* [1999] considered hydrate formation in a study of ternary nucleation, and later *Napari et al.* [2002a] incorporated a refined hydrate model in an improved theory of ternary nucleation. Recently, by carefully considering the energetics of small H_2SO_4-NH_3-H_2O clusters, *Vehkamäki et al.* [2004] demonstrated that sulfuric acid and ammonia may produce hydrate-like formations of ammonium bisulfate in vapor phase. With this supposition, *Anttila et al.* [2005] showed that the ternary nucleation rates are actually much closer to binary H_2SO_4-H_2O nucleation rates than previously thought, typically exceeding them by one or two orders of magnitude. While this undoes some of the earlier conclusions based on the efficiency of H_2SO_4-NH_3-H_2O nucleation, the new model is, nevertheless, in better agreement with observations than binary H_2SO_4-H_2O nucleation alone: and the overwhelmingly high particle production rates suggested by the earlier model are no longer a problem. *Yu* [2006b] has presented a different approach with a kinetic semiequilibrium model containing a fitted stabilizing factor to achieve a close agreement with experiments.

[5] For the atmospheric and aerosol dynamic modeling to keep abreast with the results in the forefront of nucleation research, one has to provide computationally economic yet accurate parameterizations for the models. Couple of years ago, we parameterized the binary [*Vehkamäki et al.*, 2002] and ternary [*Napari et al.*, 2002b] nucleation models, where the state-of-the-art hydrate formation scheme was employed. Along with the work of *Lucas and Akimoto* [2006], the parameterization has also been applied in the modeling works of *Gaydos et al.* [2005] and *Sotiropoulou et al.* [2006].

[6] In this paper, we present parameterizations for nucleation rate and critical cluster size and composition of the results obtained from the latest ternary H_2SO_4-NH_3-H_2O nucleation theory with the suggested effect from the ammonium bisulfate formation [*Anttila et al.*, 2005]. Parameterizations are presented in a wide range of temperatures, relative humidities, and trace gas concentrations

with the objective of accuracy and ease of use in atmospheric modeling.

2. Ternary Nucleation Model

[7] The H_2SO_4-NH_3-H_2O ternary nucleation model used in the parameterization is presented in detail in a recent paper by *Anttila et al.* [2005]. Importantly, the new model takes into account the formation of ammonium bisulfate on the nucleation rate. In the older ternary nucleation model by *Napari et al.* [2002a], only hydrate formation was accounted for. Effectively these two mechanisms play a similar role: free sulfuric acid molecules are bound to stable clusters, and the energy barrier for the formation of critical clusters with respect to these stable clusters is higher than with respect to free molecules [*Katz et al.*, 1966]. The small stable clusters can involve all free sulfuric acid and ammonia molecules or a proportion of them depending on the abundances of the three vapor species and temperature. The net effect of stable ammonium bisulfate formation, omitted from the older model, is the reduction of ternary nucleation rates by several orders of magnitude.

[8] The new ternary model is based on the classical nucleation theory that gives the work of formation of a cluster in ternary vapor [*Laaksonen et al.*, 1999] as

$$\Delta G(i,j,k) = -ik_b T \ln \frac{\rho_w^f}{\rho_{ws}^f(x_a, x_b)} - jk_b T \ln \frac{\rho_a^f}{\rho_{as}^f(x_a, x_b)}$$
$$- kk_b T \ln \frac{\rho_b^f}{\rho_{bs}^f(x_a, x_b)} + 4\pi r^2 \sigma(x_a, x_b), \qquad (1)$$

where subscripts w, a, and b stand for water, sulfuric acid, and ammonia (base) respectively, ρ^f is the number density of free molecules in ambient air, and ρ_s^f is the equilibrium-number density of vapor corresponding to liquid with composition (x_a, x_b). The cluster consists of i water, j sulfuric acid, and k ammonia molecules. Also, k_b is the Boltzmann constant, T is the temperature, r is the cluster radius, and σ is the surface tension of bulk ternary liquid. In the model, one first solves the number densities of free molecules of each three molecular species and the number densities of various stable clusters. The total density of water ρ_w^{tot} obeys

$$\rho_w^{tot} = \sum_{i>0,j,k} \rho(i,j,k), \qquad (2)$$

and a similar equation is valid for ρ_a^{tot} and ρ_b^{tot}. In the above equation, $\rho(i, j, k)$ is the density of clusters satisfying the equation

$$\rho(i,j,k) = K(i,j,k)\left(\rho_w^f\right)^i \left(\rho_a^f\right)^j \left(\rho_b^f\right)^k, \qquad (3)$$

where $K(i, j, k)$ are dimensional equilibrium constants for additions of i water, j sulfuric acid, and k ammonia molecules to a sulfuric acid molecule. $K(i, j, k)$ are taken from a thermodynamic model by *Clegg et al.* [1998]. The model by *Anttila et al.* [2005] accounts only clusters containing a maximum of two molecules of each species, and clusters with two ammonia molecules and one sulfuric acid molecule are not permitted.

[9] Once the concentration of free molecules of each species is known, the composition of the critical cluster (droplet) can be solved. Minimizing equation (1) with respect to particle numbers leads to equations

$$v_a\left(x_a^*, x_b^*\right) \ln \frac{\rho_w^f}{\rho_{ws}^f\left(x_a^*, x_b^*\right)} = v_w\left(x_a^*, x_b^*\right) \ln \frac{\rho_a^f}{\rho_{as}^f\left(x_a^*, x_b^*\right)}, \quad (4)$$

$$v_a\left(x_a^*, x_b^*\right) \ln \frac{\rho_b^f}{\rho_{bs}^f\left(x_a^*, x_b^*\right)} = v_b\left(x_a^*, x_b^*\right) \ln \frac{\rho_a^f}{\rho_{as}^f\left(x_a^*, x_b^*\right)}, \quad (5)$$

where v describes the partial molecular volume and the asterisk refers to the critical cluster. The critical cluster radius r^* is obtained by solving these equations simultaneously. The total work of formation of the critical cluster can then be solved from

$$\Delta G^* = \frac{4}{3}\pi\left(r^*\right)^2 \sigma\left(x_a^*, x_b^*\right). \quad (6)$$

[10] Note that in the model of *Anttila et al.* [2005] ΔG^* is normalized to give zero-formation energy for a sulfuric acid monomer by subtracting the classical value of $\Delta G(0, 1, 0)$ from ΔG^*. The nucleation rate is calculated from

$$J = \frac{|\lambda|/\pi}{\sqrt{-\det(\mathbf{D})/\pi}} F^e \exp\left(\frac{-\Delta G^*}{k_b T}\right), \quad (7)$$

where $\mathbf{D}$ is a matrix obtained from the second derivatives of equation (1), λ is the negative eigenvalue of matrix $\mathbf{KD}$, where $\mathbf{K}$ is the condensation matrix [*Binder and Stauffer*, 1976], and F^e is the normalization factor ensuring that a correct value for free sulfuric acid concentration is gained for $\rho(0, 1, 0)$.

[11] The new model compares well with the experimental measurements of H_2SO_4-NH_3-H_2O nucleation rates by *Ball et al.* [1999], carried out at 295.15 K, sulfuric acid concentrations between $6.5 \cdot 10^{10}$ and $1.1 \cdot 10^{11}$ cm^{-3}, ammonia mixing ratios of 80 and 170 ppt, and relative humidities of 5% and 15%; the model by *Anttila et al.* [2005] predicts between one and four orders of magnitude higher nucleation rates than experiments suggest. The predictions of the older model by *Napari et al.* [2002a] exceeded these experimental rates by 11−13 orders of magnitude. Ball et al. note that the experimental ammonia mixing ratios contain large uncertainties and are likely to be even orders of magnitude smaller than the values quoted in the region where nucleation takes place. While the new model also predicts smaller nucleation rates at smaller mixing ratios, the large experimental uncertainties in Ball et al. measurements as well as the lack of experiments on a wider range of concentrations and temperatures make a proper quantitative test of the new model impossible.

[12] The model by *Anttila et al.* [2005] relies on the use of classical nucleation theory, assigning macroscopic thermodynamical parameters to molecular size clusters. The predictive power of the classical nucleation theory is known to be somewhat limited; especially the temperature dependency of the nucleation rates is often stronger than experiments suggest. However, in spite of decades of attempts to improve the classical nucleation theory, it still presents the most

general and trustworthy theory for predicting nucleation rates in any practical application. Apart from being compromised by the assumptions inherent in classical nucleation theory, the validity of our results relies on the correctness of the activity, density, and surface tension fits. These fits have been extrapolated from a fairly limited amount of experimental data. The details of how surface tension and liquid densities are gained are given in *Korhonen et al.* [1999] and *Napari et al.* [2002a]. The vapor activities are obtained from the thermodynamic model by *Clegg et al.* [1998]. The model is valid up to a total solute molality of 40 mol/kg. Because our droplets are practically dry, we have been compelled to use the model outside its range of validity. We have carefully tested the behavior of the model from dilute solutions up the limit where only a very small amount of water is present. The resulting activity curves show no discontinuities or sudden change of slope, which could indicate a breakup of the model. It can therefore be assumed that a reasonable estimate of the vapor activities is obtained even when the total solute molality is greater than 40 mol/kg. One must however bear in mind that the application of the thermodynamic model to highly concentrated solutions adds another source of error.

[13] The classical nucleation theory with *Clegg et al.* [1998] thermodynamics automatically results the formation of ammonium bisulfate. If this phenomenon is ignored as in earlier model [*Napari et al.*, 2002a] and parameterization [*Napari et al.*, 2002b], the total concentration of sulfuric acid molecules bound into small stable clusters exceeds by many orders of magnitude the input value, which represents atmospherically realistic levels. The difference is that here we have set the total number concentration of sulfuric acid to the atmospheric input value.

[14] So far, there is no experimental evidence for or against stable ammonium bisulfate formation; small clusters consisting of a few molecules are difficult to detect, and if charged they are likely to loose ammonia ligands [*Eisele and Hanson*, 2000], and information of the original ammonia content is thus lost. Accurate quantum chemical calculations are currently the most promising route to answer the question whether the ammonium bisulfate formation is an artifact of the thermodynamic models or a real physical phenomenon. Meanwhile, we have to make sure that we use existing thermodynamical models consistently, and the main motivation of this work is to correct the former inconsistent parameterization. Binding of sulfuric acid to any stable clusters reduces the predicted nucleation rate, and thus the results predicted here can be qualitatively correct even if stable clusters with ammonia to sulfate ratio lower or higher than the ammonium bisulfate value 1:1 are formed.

3. Parameterizations of Nucleation Rate and Critical Cluster Size and Composition

[15] We present a parameterized equation for the nucleation rate $J(T, RH, c, \xi)$, where T is temperature in kelvins, RH is relative humidity given as a fraction (for example, 0.5 corresponding to 50%), c is the H_2SO_4 concentration in cm^{-3}, and ξ is the NH_3 mixing ratio in ppt. Also, the composition and size of the critical cluster are parameterized in terms of the total number of molecules $n_{tot}^*(J, T, c, \xi)$, number of sulfuric acid molecules $n_{H_2SO_4}^*(J, T, c, \xi)$, number

of ammonia molecules $n_{NH_3}^*(J, T, c, \xi)$, and radius $r^*(J, T, c, \xi)$ in nanometers.

[16] The parameterizations are valid for $T = 235-295$ K, RH $= 0.05-0.95$, $c = 5 \cdot 10^4 - 10^9$ cm^{-3}, $\xi = 0.1-1000$ ppt, and $J > 10^{-5}$ cm^{-3} s^{-1}. The lower temperature limit of 235 K corresponds to the lowest temperature for which the applied ternary nucleation model is still valid. For this temperature, a sulfuric acid concentration of at least $5 \cdot 10^4$ cm^{-3} is required, at given ranges of RH and ξ, to produce nucleation rates above the threshold value 10^{-5} cm^{-3} s^{-1}. Similarly, this threshold can be exceeded above the upper temperature limit of 295 K only when the sulfuric acid concentration is higher than 10^9 cm^{-3}. The highest nucleation rate predicted by the theory, found at the lowest temperature, highest sulfuric acid concentration, and highest ammonia mixing ratio, is approximately 10^8 cm^{-3} s^{-1}.

[17] The parameterization of J has been built by fitting 10,051 theoretical data points, covering uniformly the abovementioned regions of J, T, RH, c, and ξ, into a set of polynomial equations of T, RH, c, and ξ. These equations were found on a basis of trial and error, although third-order polynomials of temperature were expected in view of the older parameterization by *Napari et al.* [2002b]. In the fine-tuning of the nucleation-rate parameterization, a higher weight was given to a small number of data points, for which the deviation between the parameterized and theoretical rates was largest, until no data points deviated by more than about one order of magnitude in nucleation rate from the theoretical values.

[18] The resulting parameterization of the nucleation rate J has the form

$$\ln J_{fit} = -12.86185 + f_1(T)RH + f_2(T)\ln RH + f_3(T)\ln c$$
$$+ f_4(T)\ln^2 c + \frac{f_5(T)}{\ln^2 c} + f_6(T)\xi + f_7(T)\ln \xi$$
$$+ f_8(T)\ln^2 \xi + f_9(T)\ln^3 \xi + f_{10}(T)RH\ln \xi + f_{11}(T)\ln c \ln \xi$$
$$+ f_{12}(T)\frac{\ln \xi}{\ln c} + f_{13}(T)\frac{\ln RH}{\ln c} + f_{14}(T)\ln RH \ln \xi$$
$$+ \frac{f_{15}(T)}{\xi^3 \ln c} + f_{16}(T)\frac{\ln^2 \xi}{\ln c} + f_{17}(T)\frac{\ln^3 \xi}{\ln c}$$
$$+ f_{18}(T)\ln c \ln^2 \xi + f_{19}(T)\ln^2 c \ln^3 \xi + f_{20}(T)\ln RH \ln^3 \xi, \tag{8}$$

where the functions $f_i(T)$ are third-order polynomials

$$f_i(T) = a_{i0} + a_{i1}T + a_{i2}T^2 + a_{i3}T^3. \tag{9}$$

[19] The coefficients a_{ij} are listed in Table 1.

[20] The parameterization of J diverges from theoretical predictions at nucleation rates lower than 10^{-5} cm^{-3} s^{-1}. It can even wrongly produce significant nucleation rates at very low concentrations. We have prevented this problem by parameterizing an onset temperature T_{onset} for nucleation rate of $5 \cdot 10^{-6}$ cm^{-3} s^{-1} as a function of RH, c, and ξ. It is given by

$$T_{onset} = 143.600 + 1.01789RH + 10.1964\ln c - 0.184988\ln^2 c$$
$$- 17.1618\ln \xi + 109.9247\frac{\ln \xi}{\ln c} + 0.773412\ln c \ln \xi$$
$$- 0.155764\ln^2 \xi. \tag{10}$$

Table 1. Coefficients of Polynomials $f_i(T)$[a]

i	a_{i0}	a_{i1}	a_{i2}	a_{i3}
1	−358.234	4.86304	−0.0217555	0.0000321287
2	−980.923	10.0542	−0.0330664	0.0000342740
3	1200.47	−17.3711	0.0817068	−0.000125345
4	−14.8330	0.293263	−0.00164975	2.84407E−6
5	−4.39129E6	56383.9	−239.836	0.337651
6	4.90553	−0.0546302	0.000202584	−2.50241E−7
7	−231376	2919.29	−12.2865	0.0172493
8	75061.2	−931.880	3.86327	−0.00534947
9	−3180.56	39.0827	−0.160485	0.000220314
10	−100.216	0.977887	−0.00305118	2.96732E−6
11	5599.91	−70.7090	0.297880	−0.000418665
12	2.36093E6	−29752.1	125.050	−0.175300
13	16597.8	−175.237	0.603322	−0.000673179
14	−89.3896	1.15334	−0.00495455	7.09631E−6
15	−629.788	7.77281	−0.0319741	0.0000438376
16	−732007	9100.06	−37.7711	0.0523546
17	40751.1	−501.670	2.06347	−0.00283687
18	−1911.03	23.6904	−0.0980787	0.000135646
19	2.79231	−0.0342255	0.000140192	−1.92012E−7
20	3.17121	−0.0378223	0.000150056	−1.98284E−7

[a]Read $E-x$ as 10^{-x}.

[21] If T_{onset} exceeds the temperature of interest, the nucleation rate is less than $5 \cdot 10^{-6}$ cm^{-3} s^{-1} and should be set to zero, and equation (8) cannot be used.

[22] The parameterizations for critical cluster radius $r^*(J, T, c, \xi)$ (in nanometers), total number of molecules $n_{tot}^*(J, T, c, \xi)$, number of sulfuric acid molecules $n_{H_2SO_4}^*(J, T, c, \xi)$, and number of ammonia molecules $n_{NH_3}^*(J, T, c, \xi)$ are

$$r^* = 0.328886 - 0.00337417T + 0.0000183474T^2$$
$$+ 0.00254198\ln c - 0.0000949811T\ln c$$
$$+ 0.000744627\ln^2 c + 0.0243034\ln \xi + 0.0000158932T\ln \xi$$
$$- 0.00203460\ln c \ln \xi - 0.000559304\ln^2 \xi$$
$$- 4.88951 \cdot 10^{-7}T\ln^2 \xi + 0.000138470\ln^3 \xi$$
$$+ 4.14108 \cdot 10^{-6}\ln J - 0.0000268131T\ln J$$
$$+ 0.00128791\ln \xi \ln J - 3.80352 \cdot 10^{-6}T\ln \xi \ln J$$
$$- 0.0000187902\ln^2 J, \tag{11}$$

$$n_{tot}^* = 57.4009 - 0.299634T + 0.000739548T^2 - 5.09060\ln c$$
$$+ 0.0110166T\ln c + 0.0675003\ln^2 c - 0.810283\ln \xi$$
$$+ 0.0159051T\ln \xi - 0.204417\ln c \ln \xi + 0.0891816\ln^2 \xi$$
$$- 0.000496903T\ln^2 \xi + 0.00570439\ln^3 \xi + 3.40987\ln J$$
$$- 0.0149170T\ln J + 0.0845909\ln \xi \ln J$$
$$- 0.000148006T\ln \xi \ln J + 0.00503805\ln^2 J, \tag{12}$$

$$n_{H_2SO_4}^* = -4.71542 + 0.134364T - 0.000471847T^2$$
$$- 2.56401\ln c + 0.0113533T\ln c + 0.00108019\ln^2 c$$
$$+ 0.517137\ln \xi - 0.00278825T\ln \xi + 0.806697\ln^2 \xi$$
$$- 0.00318491T\ln^2 \xi - 0.0995118\ln^3 \xi$$
$$+ 0.000400728T\ln^3 \xi + 1.32765\ln J - 0.00616765T\ln J$$
$$- 0.110614\ln \xi \ln J + 0.000436758T\ln \xi \ln J$$
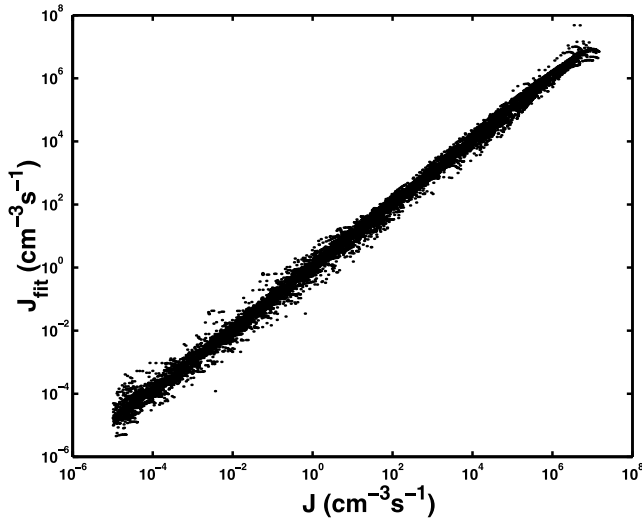$$+ 0.000916366\ln^2 J, \tag{13}$$

Figure 1. Comparison between the theoretical nucleation rates J (x axis) and the parameterized nucleation rates J_{fit} (y axis) for 10,051 data points covering uniformly the validity regions of the parameterization.

$$
\begin{aligned}
n^*_{\text{NH}_3} =\ & 71.2007 - 0.840960T + 0.00248030T^2 + 2.77986 \ln c \\
& - 0.0147502T \ln c + 0.0122645 \ln^2 c - 2.00993 \ln \xi \\
& + 0.00868912T \ln \xi - 0.00914118 \ln c \ln \xi + 0.137412 \ln^2 \xi \\
& - 0.000625323T \ln^2 \xi + 0.0000937733 \ln^3 \xi \\
& + 0.520297 \ln J - 0.00241987T \ln J \\
& + 0.0791639 \ln \xi \ln J - 0.000302159T \ln \xi \ln J \\
& + 0.00469770 \ln^2 J,
\end{aligned} \tag{14}
$$

where J is the parameterized nucleation rate. The validity regions for these parameterizations are the same as for the nucleation rate parameterization. The water content in the critical cluster was not parameterized; usually, the number of water molecules in the critical cluster is very close to zero. However, whenever the subtraction of $n^*_{\text{H}_2\text{SO}_4}$ and $n^*_{\text{NH}_3}$ from n^*_{tot} produces a number significantly greater than zero, it can be considered as a reasonable estimate for the number of water molecules in the critical cluster.

[23] Additionally, we have parameterized the threshold concentration of sulfuric acid (1/cm^3) which produces a nucleation rate $J = 1/(\text{cm}^3\ \text{s})$. It is given by

$$
\begin{aligned}
\ln c^{J=1} =\ & -40.5988 + 5.00845/\xi + 0.00995956\xi + 0.231207T \\
& - (0.0191883T)/\xi - 0.0000312301T\xi + 15.4213 \ln \xi \\
& - 0.0636755T \ln \xi - 3.48925 \ln^2 \xi + 0.0143679T \ln^2 \xi \\
& + 0.234708 \ln^3 \xi - 0.000995330T \ln^3 \xi.
\end{aligned} \tag{15}
$$

4. Results

[24] We illustrate the comparison between the parameterized nucleation rates and the theoretical values in Figure 1. This figure shows all 10,051 values used in the construction of the parameterization, uniformly distributed in $T = 235$–295 K, RH = 0.05–0.95, $c = 5 \cdot 10^4$–10^9 cm^{-3} and $\xi = 0.1$–1000 ppt. The one-to-one line corresponding to a perfect fit exhibits the highest concentration of points. For the ratio J/J_{fit}, 68% of all values are in the range 0.67–1.51,
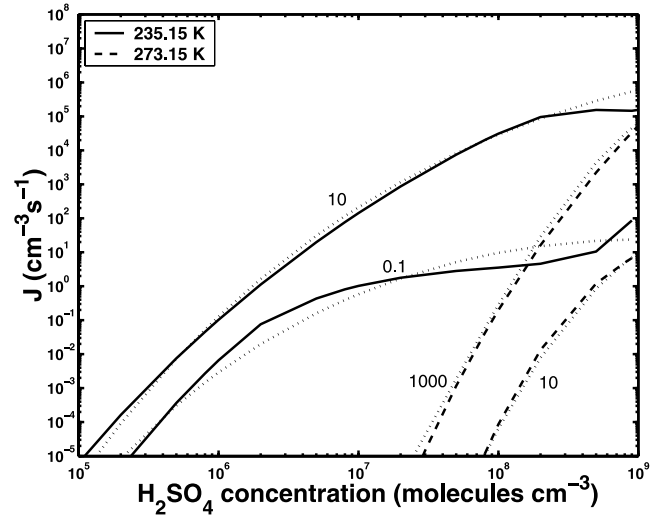

Figure 2. Theoretical nucleation rates J (full and dashed line) and the parameterized nucleation rates J_{fit} (dotted line) as functions of total sulfuric acid concentration in the vapor. The corresponding ammonia mixing ratios (in ppt) are indicated for each curve, while RH = 50% for all curves. The full and dashed curves correspond to temperatures of 235.15 and 273.15 K respectively.

95% in the range 0.38–2.63, and 99.8% in the range 0.10–10.00. We have carefully checked that this accuracy holds indeed for the entire region, and not just for data points used to construct the parameterization. Thus, one can safely assume that for the entire range the parameterized nucleation rates are accurate to one order of magnitude. We stress that outside these regions the parameterization may deviate rapidly from the theory, as typical for polynomial fits.

[25] Figures 2, 3 and 4 demonstrate the behavior of the theoretical and parameterized nucleation rates as functions
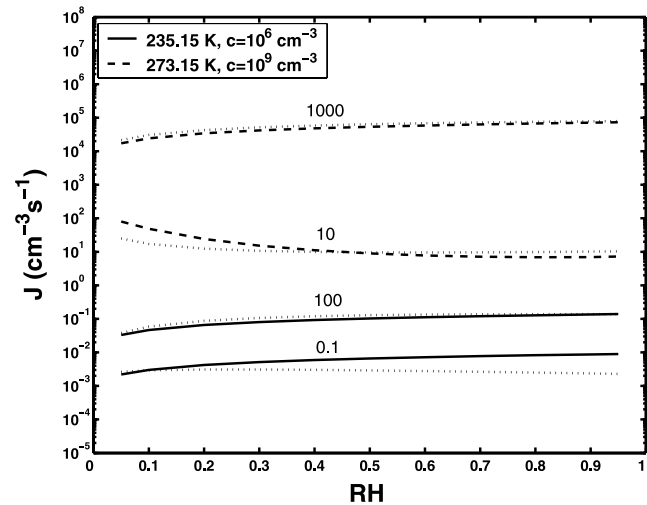

Figure 3. Theoretical nucleation rates J (full and dashed lines) and the parameterized nucleation rates J_{fit} (dotted lines) as functions of relative humidity at $T = 235.15$ K with H$_2$SO$_4$ concentration of 10^6 cm^{-3} (full lines) and at $T = 273.15$ K with H$_2$SO$_4$ concentration of 10^9 cm^{-3} (dashed lines). The corresponding ammonia mixing ratios (in ppt) are indicated for each curve.
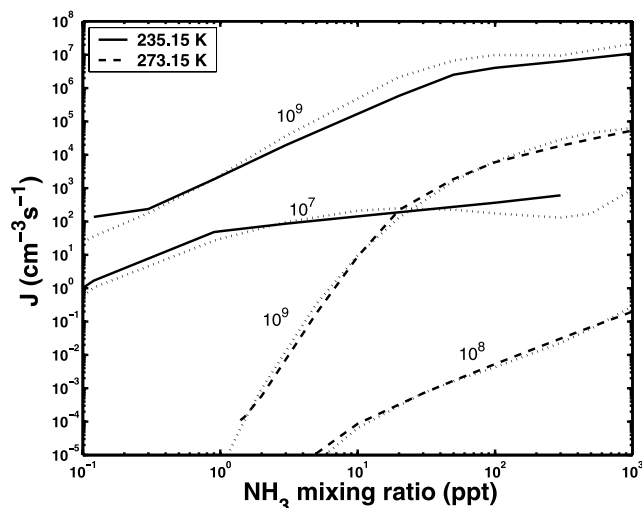
Figure 4. Theoretical nucleation rates J (full and dashed lines) and the parameterized nucleation rates J_{fit} (dotted line) as functions of ammonia mixing ratio at $T = 235.15$ K (full lines) and at $T = 273.15$ K (dashed lines). The corresponding sulfuric acid concentrations (in molecules cm^{-3}) are indicated for each curve, while RH = 50% for all curves.

of c, RH, and ξ at $T = 235.15$ K and $T = 273.15$ K. Figure 2 illustrates how the sulfuric acid concentration affects the theoretical and parameterized nucleation rates. At 235.15 K, in other words at the lower temperature limit, the parameterization deviates from theoretical predictions more than in the mid-temperature range at 273.15 K. This deviation becomes more pronounced at large sulfuric acid concentrations but is always, however, less than one order of magnitude in nucleation rate.

[26] The theoretical and parameterized nucleation rates are displayed in Figure 3 as functions of relative humidity. The figure indicates that the ternary nucleation rate is generally a weak function of RH. On one hand, elevated RH boosts the formation of sulfuric hydrates, which in turn stabilize the vapor and attenuate nucleation. On the other hand, higher RH lowers the formation energy of the critical cluster. The trade-off between the two effects determines how ternary nucleation rate varies with RH. The parameterization captures the net effect fairly accurately.

[27] The nucleation rate as a function of ammonia mixing ratio is presented in Figure 4. Again, the parameterization deviates from theoretical values more at 235.15 K than at 273.15 K. All theoretical curves in the figure do not span the entire region of ammonia mixing ratios. Indeed, at some specific values of vapor concentration and temperature, the ternary theory breaks up. The breakup can be caused by several reasons, for example, the calculation of the nucleation rate requires a negative eigenvalue of the **KD** matrix, which cannot always be found. The fit provides a reliable interpolation scheme for J also when the full thermodynamic theory fails because of numerical problems.

[28] Figure 5 illustrates the temperature dependencies of the theoretical and parameterized nucleation rates. The variation of nucleation rate with temperature is strongest at low nucleation rates. The nucleation rate increases with

decreasing temperature at constant H_2SO_4 concentration. However, at high H_2SO_4 concentration, the nucleation rate reaches a plateau at low temperatures. The parameterization compares well with the theoretical values throughout the whole temperature range, although minor deviations can be seen at the low-temperature end. The top curve in Figure 5 corresponds to highest nucleation rates obtained with the parameterization. Thus, within the validity regions of the parameterization, significant ternary nucleation does not occur at temperatures higher than 295 K. We note that, outside the regions of our parameterization, the ammonia mixing ratio of 10,000 ppt cannot trigger significant nucleation above 295 K unless the sulfuric acid concentration is at least 10^9 cm^{-3}.

[29] In Figures 6, 7, 8 and 9, the theoretical predictions of critical cluster size and composition are compared with parameterizations presented in equations 11, 12, 13 and 14. Figure 6 compares the theoretical and parameterized critical cluster radii r^*. For the ratio r/r_{fit}, 68% of the all values are in the range 0.989–1.012 and 95% in the range 0.975–1.025. The parameterization is accurate both for small and large cluster radii. Figures 7, 8, and 9 present the accuracy of the parameterizations of the total number of molecules n^*_{tot}, number of H_2SO_4 molecules $n^*_{H_2SO_4}$, and number of NH_3 molecules $n^*_{NH_3}$, respectively. The maximum deviation between the theoretical and parameterized n^*_{tot} is approximately 20%. Somewhat larger maximum deviations from theoretical values are exhibited by $n^*_{H_2SO_4}$ and $n^*_{NH_3}$ parameterizations. In particular, the parameterization of $n^*_{NH_3}$ sometimes produces too large numbers of ammonia molecules in small critical clusters. Generally, however, our parameterizations give good approximations for the critical cluster composition.

[30] Computationally, calculations of parameterized nucleation rates, critical cluster sizes and critical cluster
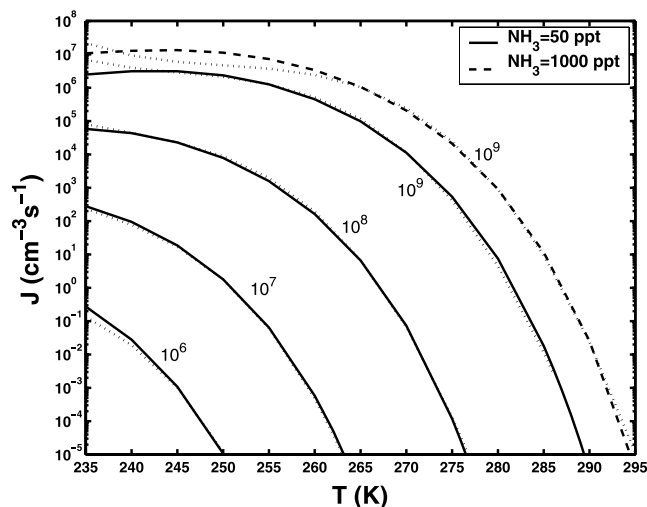

Figure 5. Theoretical nucleation rates J (full and dashed lines) and the parameterized nucleation rates J_{fit} (dotted lines) as functions of temperature with ammonia mixing ratios of 50 (full lines) and 1000 ppt (dashed line). The corresponding sulfuric acid concentrations (in molecules cm^{-3}) are indicated for each curve, while RH = 50% for all curves.
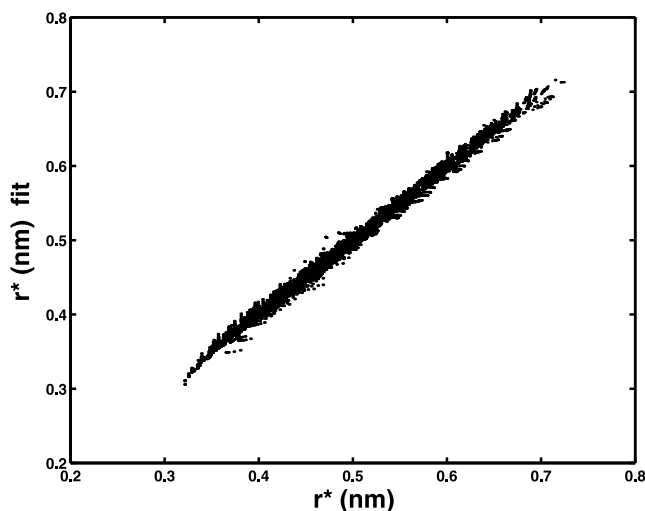
Figure 6. Comparison between the theoretical critical cluster radii r^* (x axis) and the corresponding parameterized radii r^*_{fit} (y axis) for 10,051 data points covering uniformly the validity regions of the parameterization.

Figure 8. Comparison between the theoretical number of sulfuric acid molecules in the critical cluster $n^*_{\mathrm{H_2SO_4}}$ (x axis) and the corresponding parameterized number of sulfuric acid molecules $n^*_{\mathrm{H_2SO_4,fit}}$ (y axis).

compositions are by a factor of 10^5 more efficient than the calculations with the full thermodynamical model presented by *Anttila et al.* [2005].

[31] Equation (15) gives a parameterized equation for the threshold concentration of sulfuric acid which produces the nucleation rate 1/(cm^3 s). The equation neglects the effect of relative humidity to nucleation rate. The ratio between the theoretical and parameterized concentrations is between 0.3 and 3; thus, the equation serves mainly as a quick approximation of the required threshold concentration. A more accurate parameterization would require a much more complex equation than the one presented here. For a more accurate calculation of the threshold concentration of sulfuric acid, we recommend the use of equation (8).
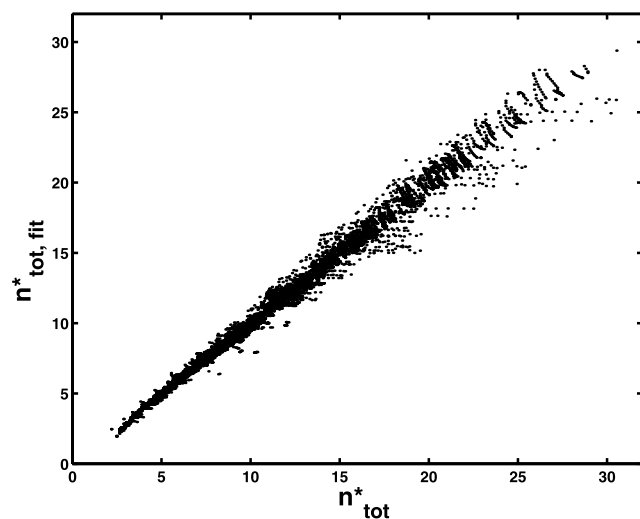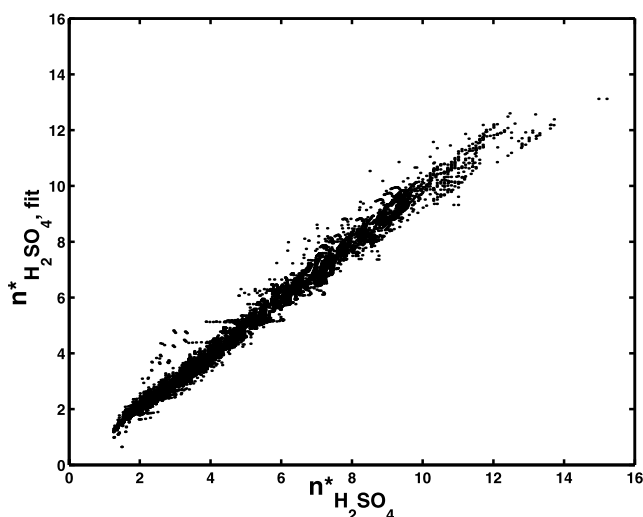
[32] The calculations of threshold values indicate the conditions where the new ternary nucleation theory predicts atmospherically significant nucleation rates. For example, at $T = 235$ K and $\xi = 0.1-10$ ppt corresponding to conditions found at the upper troposphere, $c^{J=1} = 10^6$ to 10^7 1/(cm^3), and at $T = 273-283$ K and $\xi = 1000$ ppt corresponding to polluted conditions in the lower troposphere, $c^{J=1} = 10^8$ to $5 \cdot 10^8$ 1/(cm^3).

5. Conclusions

[33] We have constructed parameterizations for critical droplet radius, number of molecules in the cluster, and nucleation rate in homogeneous ternary H$_2$SO$_4$-NH$_3$-H$_2$O nucleation. The parameterizations are based on a very recent

Figure 7. Comparison between the theoretical total number of molecules in the critical cluster n^*_{tot} (x axis) and the corresponding parameterized total number of molecules $n^*_{\mathrm{tot,fit}}$ (y axis).
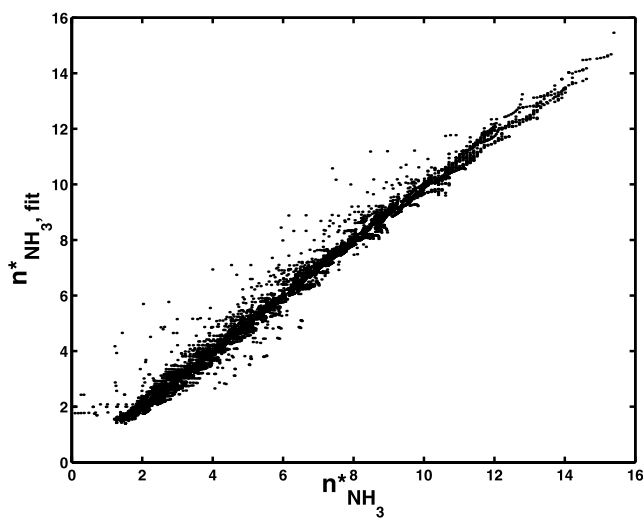

Figure 9. Comparison between the theoretical number of ammonia molecules in the critical cluster $n^*_{\mathrm{NH_3}}$ (x axis) and the corresponding parameterized number of ammonia molecules $n^*_{\mathrm{NH_3,fit}}$ (y axis).

nucleation model incorporating both sulfuric acid hydrate and ammonium bisulfate formation in the vapor phase. The parameterized quantities are presented as polynomial functions of temperature, relative humidity, and vapor phase concentrations or logarithms of these values.

[34] The parameter values cover those typically found in the troposphere. In particular, compared with our earlier parameterization [*Napari et al.*, 2002b], we have extended the range of ammonia concentrations to 1000 ppt, which enables the use of the parameterizations in heavily polluted areas. The parameterization reproduces the model values of nucleation rate within an order of magnitude for nucleation rates above 10^{-5} cm^{-3} s^{-1}. The greatest deviations are found at lowest temperatures.

[35] The old parameterization by *Napari et al.* [2002b] predicted nucleation practically everywhere and all the time in the troposphere. The nucleation rates from the new parameterization are several orders of magnitude lower, which is in line with observations. According to the new model, the conditions for significant ternary nucleation rates are most likely to be found in the upper troposphere. Significant nucleation rates can also take place at the lower troposphere if the concentrations of sulfuric acid and ammonia are extremely high.

[36] The possible sources of error in the new model, and thus also in the parameterization, are the known problems of applying thermodynamic theory to small critical clusters and the fact that, at the present state, also the ammonium bisulfate formation scheme relies on classical droplet model. Moreover, the values used of the activities, densities, and surface tensions of the ternary solution required for the use of classical nucleation theory are bound to be somewhat approximate, as discussed in detail in the section describing the thermodynamic model. Also, the relative importance of the different nucleation routes in the atmosphere is still under discussion. Nevertheless, the new parameterization presents a significant improvement on the old one and should yield more realistic rates of particle formation in atmospheric modeling.

[37] Finally, we would like to point out that, when incorporating a nucleation parameterization, such as the one developed here, into a large-scale model, the parameterization should be coupled with a new particle formation parameterization (e.g., *Kerminen and Kulmala* [2002]; *Kerminen et al.* [2004]) rather than inserting freshly nucleated clusters directly into the smallest size bin or mode. Otherwise large errors are induced to the predicted new particle formation rates because of a relatively crude representation of the aerosol dynamics in such models.

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T. Anttila, Finnish Meteorological Institute, Research and Development, P.O. Box 503, Helsinki, FIN-00101 Finland.

M. Kulmala, J. Merikanto, I. Napari, and H. Vehkamäki, Department of Physical Sciences, University of Helsinki, P.O. Box 64, Helsinki, FIN-00014 Finland. (joonas.merikanto@helsinki.fi)