Parameterization of ammonia and water content of atmospheric droplets with fixed number of sulfuric acid molecules

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Abstract

We present a parameterization for numbers of water and ammonia molecules in an equilibrium droplet with fixed number of sulfuric acid molecules at known relative humidity, ammonia mixing ratio and temperature. The radius of the droplet is also parameterized. The parameterizations are based on macroscopic model of solution droplets and up-to-date thermodynamics. The binary parameterizations are valid for temperatures 190–330 K and relative humidities 1–99%. The ternary parameterization can be used at temperatures 240–300 K, relative humidities 5–95%, and ammonia mixing ratios 10^{-4}–100 ppt. In both cases the parameterizations are valid for droplets containing up to 10^{11} sulfuric acid molecules. The droplet composition is always between the limits of pure ammonium bisulfate and pure ammonium sulfate.

1. Introduction

Atmospheric aerosol particles influence the Earth's radiation balance directly by scattering and absorbing solar radiation, and indirectly by acting as cloud condensation nuclei (CCN) (see e.g. Charlson et al., 1992; Stott et al., 2000; Ramanathan et al., 2001; Menon et al., 2002). During the recent years it has become obvious that homogeneous nucleation events of fresh aerosol particles take frequently place in the atmosphere, and that particle formation and subsequent growth might have a significant role in determining atmospheric aerosol load (see Kulmala et al., 2004 and references therein). In order to be able to quantify this we need to perform

studies on formation and growth of atmospheric aerosols including a) formation of their gaseous precursors b) related micrometeorology, c) atmospheric chemistry, and d) atmospheric phase transitions. The general approach includes both experimental (laboratory and field experiments) and theoretical (basic theories, simulations, model development) approaches.

A typical way to investigate atmospheric aerosol dynamics is aerosol dynamic modeling. In the models different aerosol processes and different aerosol compounds are described (see e.g. Korhonen et al., 2004). Often complex processes like nucleation are parameterized in models. Due to its complexity, analyzing aerosol (liquid or solid) phase thermodynamics is often the task demanding most computer power (see e.g. Clegg et al., 1998). Particularly, relevant connections between dynamic aerosol processes like nucleation and condensation and thermodynamics are

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needed, since e.g. the vapor pressure difference between aerosol surface and the gas phase has to be known.

Aerosol dynamic modeling (nucleation, condensation, coagulation, deposition, cloud processes) with gas phase chemistry model calculations are performed to obtain the atmospheric significance of different chemical compounds (e.g. Korhonen et al., 2004; Lehtinen and Kulmala, 2003). In these models sink terms for condensable molecules are evaluated from aerosol formation, and growth processes and the source terms are obtained from gas phase chemistry. The effect of ions on aerosol dynamics and particularly on the growth rate have also been investigated (Laakso et al., 2004).

In our earlier papers (Vehkamäki et al., 2002; Napari et al., 2002c) we presented parameterizations for critical nuclei in sulfuric acid+water and sulfuric acid+ammonia+water systems. In this work we aim to parameterize the properties of larger droplets for use e. g. in aerosol dynamics. One important variable in aerosol dynamics is particle size. Quite often the dry size of particles is known, although in reality the wet size (i.e. the size corresponding ambient conditions) determines the atmospheric effects of the particle. In the present paper we investigate the wet size of aerosol particles in binary (sulfuric acid+water) and ternary (sulfuric acid+ammonia+water) systems as a function of ambient conditions. In practice we establish the wet size as a function of dry size or number of sulfuric acid molecules in the particle. For computational efficiency, we have developed straightforward parameterizations for the wet size.

2. Model

The treatment of the binary and ternary droplets relies on the Köhler description of solution droplets (see e. g. Seinfeld and Pandis, 1998). We are interested in finding droplets with a certain number of molecules of sulfuric acid N_a; this procedure involves solving the Kelvin equation together with the condition of constant number of acids:

$$\frac{A_{wg}(x_a)}{A_{wl}(x_a)} = \exp\left(\frac{2v_w(x_a)\sigma(x_a)}{k_B T R}\right) \tag{1}$$

$$N_a = \text{const}, \tag{2}$$

where A_{wg} and A_{wl} are the vapor and liquid phase activities of water, $v(x_a)$ is the partial molecular volume of water in the solution with sulfuric acid mole fraction x_a, $\sigma(x_a)$ is the surface tension of the solution, R is the radius of the droplet, k_B is Boltzmann's constant, and T is temperature. Once the mole fraction is found, the

droplet radius is obtained from Eq. (1). The number of molecules of compound i in the cluster is given by

$$N_i = N_{il} + N_{is}, \tag{3}$$

where the core number of molecules N_{il} is obtained from

$$N_{il} = \frac{4\pi R^3 x_i/3}{x_a v_a(x_a) + (1-x_a)v_w(x_a)} \tag{4}$$

and the surface excess number of molecules N_{as} is calculated as by Noppel et al. (2002):

$$N_{is} = \frac{4\pi r^2 \frac{d\sigma}{dx_a}}{\frac{v_i}{v_j}\frac{d\mu_j l}{dx_a} - \frac{d\mu_i l}{dx_a}} \tag{5}$$

with $i \neq j$. Here $\mu_{il} = \mu_{il}(p_l, x_a)$ is the chemical potential of component i in the uniform liquid core with sulfuric acid mole fraction x_a and pressure p_l.

In the ternary case, the droplet is assumed to be in equilibrium with both the water and ammonia vapors. Two simultaneous Kelvin equations are then written for the droplet which, because radius and surface tension are the same in both the equations, reduce to (with the additional condition of constant N_a)

$$v_b(x_a, x_b)\ln\left(\frac{A_{wg}(x_a, x_b)}{A_{wl}(x_a, x_b)}\right)$$
$$= v_w(x_a, x_b)\ln\left(\frac{A_{bg}(x_a, x_b)}{A_{bl}(x_a, x_b)}\right) \tag{6}$$

$$N_a = \text{const}, \tag{7}$$

where the lower index b ("base") refers to ammonia. The number of molecules of type i is obtained as the sum of core and surface excess terms in a similar fashion as in the binary case.

The thermodynamics needed to calculate the liquid phase activities, density, and surface tension of the solution are the same as in our earlier model studies (Noppel et al., 2002; Napari et al., 2002b). The binary liquid phase activities are obtained from the model of Zeleznik (1991). The ternary activities are calculated using the model of Clegg et al. (1998) (see also http://www.hpc1.uea.ac.uk/~e770/aim.html). This model of restricted to non-alkaline solutions; however, earlier calculations with a different model (Korhonen et al., 1999) suggested that the amounts of alkaline clusters are probably very small.

Note that in this paper we give the properties of the equilibrium droplet with set number of sulfuric acid molecules, relative humidity and ammonia mixing ratio.

Parameterizations for properties of critical cluster, which is the equilibrium droplet with set sulfuric acid vapor phase concentration, relative humidity, ammonia mixing ratio, and nucleation rate can be found in (Vehkamäki et al., 2002; Napari et al., 2002c), Noppel et al. (2002) and Napari et al. (2002b).

3. Parameterizations

The parameterized quantities are the radius of the solution droplet R and the number of water and ammonia molecules, N_w and N_b. The given parameters are temperature T, relative humidity (RH), ammonia mixing ratio (ξ), and the number of sulfuric acid molecules N_a. In the first approximation all these quantities are linearly dependent on the number of acid molecules on the logarithmic scale; however, the dependencies on the other parameters are more complicated. To find proper fitting functions we followed the same strategy as in our nucleation rate parameterizations, i. e. we kept all variables constant at a time except one and made a set of "partial" parameterizations which served as a guideline to parameterization of an additional variable, etc. During this process cross terms appeared, the amount of which we tried to keep to minimum. Also, we did not include terms of unnecessarily high degree to avoid unintentional undulation in the fitted curves.

We tried to make the parameterizations applicable to a broad range of atmospheric conditions within the limits of validity of the thermodynamic models. Even so, we had to limit the allowed parameter ranges somewhat to reduce the deviations from the model results to an acceptable level. The binary parameterizations are valid at temperatures between 190 and 330 K, relative humidities between 1% and 99%, and number acid molecules in the droplet from 2 to 10^{11}. The corresponding limits for the ternary parameterization are $T = 240$–300 K, $RH = 5$–95%, and $N_a = 1$–10^{11} molecules. The mixing ratio of ammonia may vary between 10^{-4} and 100 ppt.

In some cases the ternary model exhibited odd behavior: at certain parameter values the number of water or ammonia molecules turned out to be negative due to large negative values of the surface excess numbers. This implicates breakdown of the classical droplet model; similar observations has been done in nucleation calculations of water–sulfuric acid–ammonia system (Napari et al., 2002b) as well as in other systems containing water and inorganic acids (Napari et al., 2002a). To place the parametrization on a physically sound basis we required that the surface excess contribution is a minor correction to the core molecular number for each molecular species $|N_{is}/N_{il}| < 0.5$.

The radius of the wet particle (in nanometers) can be calculated in the binary case from

$$
\begin{aligned}
R_{\mathrm{bin}}[\mathrm{nm}] = (10^9)\exp(&-21.725908 + 0.337092A_{\mathrm{wg}} - 0.986496\,A_{\mathrm{wg}}^2 \\
&+ 0.617096\,A_{\mathrm{wg}}^3 - 0.000250T + 0.000435\,A_{\mathrm{wg}}T \\
&+ 0.349305\log(N_a) + 0.008631\,A_{\mathrm{wg}}\log(N_a) \\
&+ 0.043999\,A_{\mathrm{wg}}^2\log(N_a) - 0.000014\,T\log(N_a) \\
&- 0.001047\log(N_a)^2 - 0.000364\,A_{\mathrm{wg}}\log(N_a)^2 \\
&+ 0.000024\log(N_a)^3 - 0.189518\log(N_a)^{-3} \\
&+ 0.505239\log(N_a)^{-2} - 0.414451\log(N_a)^{-1} \\
&- 0.006132\,A_{\mathrm{wg}}\log(N_a)^{-1} - 0.000935\,A_{\mathrm{wg}}^2\log(N_a)^2 \\
&+ 0.022998\log(A_{\mathrm{wg}}) + 0.000804\,A_{\mathrm{wg}}^{-1}\log(N_a)^{-1})
\end{aligned}
$$

(8)

Here the gas-phase activity of water is obtained from $A_{wg} = RH/100$, where RH is relative humidity. Temperature is expressed in Kelvins.

In the ternary case

$$
\begin{aligned}
R_{\mathrm{ter}}[\mathrm{nm}] = \exp(&-0.639278 - 0.284986A_{wg} - 4.015855A_{wg}^2 \\
&+ 3.284256A_{wg}^3 - 0.001121T + 0.002738A_{wg}T \\
&+ 0.091411\log(\xi) - 0.012385A_{wg}\log(\xi) \\
&- 0.000314T\log(\xi) + 0.014860\log(\xi)^2 \\
&+ 0.295729\log(N_a) + 0.092901A_{wg}\log(N_a) \\
&- 0.000013T\log(N_a) - 0.000014\log(\xi)\log(N_a) \\
&+ 0.001275\log(N_a)^2 - 0.002414A_{wg}\log(N_a)^2 \\
&- 0.000006\log(N_a)^3 + 1.411983/(2.152773 \\
&+ 0.271051A_{wg}^{-3.355955}) - 1.816682/(9.187502 \\
&+ 0.003344\log(N_a)^{4.634970}) - 0.000026\log(\xi)^3 \\
&- 0.363925/(20 + 1.499757\log(\xi)) \\
&+ 0.000343\log(\xi)^3/(1 + 58.724932A_{wg}) \\
&- 0.005554\log(\xi)^2 T^{0.158226} - 0.001342\log(\xi)^2 A_{wg}^{4.073993} \\
&- 0.000048\log(A_{wg})^{6.361476} - 0.000876TA_{wg}^3),
\end{aligned}
$$

(9)

where ξ is the ammonia mixing ratio (in ppt).

The number of water molecules in the binary droplet is obtained from

$$
\begin{aligned}
N_{\mathrm{w,bin}} = {}& 2.347253 + 0.685492A_{\mathrm{wg}} - 3.206742A_{\mathrm{wg}}^2 + 2.091986A_{\mathrm{wg}}^3 \\
&- 0.002885T + 0.003298A_{\mathrm{wg}}T + 1.042857\log(N_a) \\
&+ 0.062866A_{\mathrm{wg}}\log(N_a) + 0.109673A_{\mathrm{wg}}^2\log(N_a) \\
&- 0.000046T\log(N_a) - 0.003419\log(N_a)^2 \\
&- 0.002128A_{\mathrm{wg}}(\log(N_a)^2) + 0.000085\log(N_a)^3 \\
&- 1.075758\log(N_a)^{-3} + 3.001545\log(N_a)^{-2} \\
&- 2.646603\log(N_a)^{-1} - 0.149366A_{\mathrm{wg}}\log(N_a)^{-1} \\
&- 0.002155A_{\mathrm{wg}}^2\log(N_a)^2 + 0.173433\log(A_{\mathrm{wg}}),
\end{aligned}
$$

(10)

whereas in the ternary droplet

$$
\begin{aligned}
N_{w,ter} = \exp(&-2.087083 - 2.622092 A_{wg} - 2.389878 A_{wg}^2 \\
&+ 3.193793 A_{wg}^3 + 0.017040T + 0.005723 A_{wg}T \\
&+ 0.932554 \log(\xi) - 0.046003 A_{wg} \log(\xi) \\
&- 0.003507\ T\log(\xi) + 0.030511 \log(\xi)^2 \\
&+ 2.192944 \log(N_a) + 0.384795 A_{wg}\log(N_a) \\
&- 0.000925\ T\log(N_a) + 0.002217 \log(\xi)\log(N_a) \\
&- 0.062972 \log(N_a)^2 - 0.010785 A_{wg}\log(N_a)^2 \\
&+ 0.001314 \log(N_a)^3 - 1.842170/(0.496611 \\
&+ 0.934700 A_{wg}^{0.929353}) - 0.000693/(-1.970018 \\
&+ 1.753037 \log(N_a)^{0.143862}) - 0.000209 \log(\xi)^3 \\
&- 1.621097/(20 + 1.649315 \log(\xi)) \\
&+ 0.010454(\log(\xi)^3)/(1 + 206.108274 A_{wg}) \\
&- 0.000001 (\log(\xi)^2) T^{1.641722} - 0.018328 (\log(\xi)^2) A_{wg}^{1.765341} \\
&+ 4.911091 (\log(A_{wg}))^{0.274097} - 0.010868\ T A_{wg}^3).
\end{aligned}
\tag{11}
$$

Finally, the number of ammonia molecules can be calculated from

$$
\begin{aligned}
N_b = \exp(&-7.346864 + 24.326049 A_{wg} - 2.623078 A_{wg}^2 \\
&+ 1.056830 A_{wg}^3 + 0.027181\ T - 0.085010 A_{wg}T \\
&- 2.381617 \log(\xi) + 0.572576 A_{wg}\log(\xi) + 0.008097\ T\log(\xi) \\
&- 0.027622 \log(\xi)^2 + 1.205401 \log(N_a) - 0.049493 A_{wg}\log(N_a) \\
&- 0.000418\ T\log(N_a) + 0.002387 \log(\xi)\log(N_a) \\
&- 0.006330 \log(N_a)^2 + 0.001445 A_{wg}\log(N_a)^2 + 0.000132 \log(N_a)^3).
\end{aligned}
\tag{12}
$$

4. Comparison of the model data and the parameterizations

We first present plots showing the ratios of parameterized and model values in order to assess the overall goodness of the parameterizations. Fig. 1 shows the maximum and minimum limits of the ratios of the parameterized values (fit) and model results for the binary system. Limits for both the number of water molecules and the droplet radius are shown as a function of relative humidity. It can be seen that parameterizations reproduce the original values quite well at low and medium *RH* but at high *RH* the discrepancies are much larger. The increased scatter at high *RH* is related to the more significant deviations from linearity of the parameterizations as the solution of Eq. (1) approaches bifurcation point at *RH* = 100%, above which the equilibrium conditions are satisfied with not one, but two droplet sizes, the larger of which represents an unstable equilibrium. 93.2% of the ratios N_w(fit)/N_w(model) are in the range 0.83–1.2. The corresponding percentage for R(fit)/R(model) is 99.3%.

Fig. 2 depicts the ratio R(fit)/R(model) for the ternary system as a function of the modeled particle wet radius. The accuracy of the parameterization is comparable to the binary one: 99.7% of the ratios are within 0.83–1.2. In contrast to binary droplets, the points showing largest deviation from modeled values are not generally those corresponding to high relative humidity.

The temperature dependence is not easily parameterized. Both the particle radius and the numbers of molecules show nonlinear behavior as a function temperature. However, the parameterizations are able to follow the temperature variations in an average manner and, therefore, the deviations from the model values are never large.

A comparison of the parameterized numbers of water and ammonia molecules with the model data for the ternary system is presented in Fig. 3. Here, the parameterizations are less accurate than in the binary case of Fig. 1. Still, 73% of the ratios N_w(fit)/N_w(model) are in
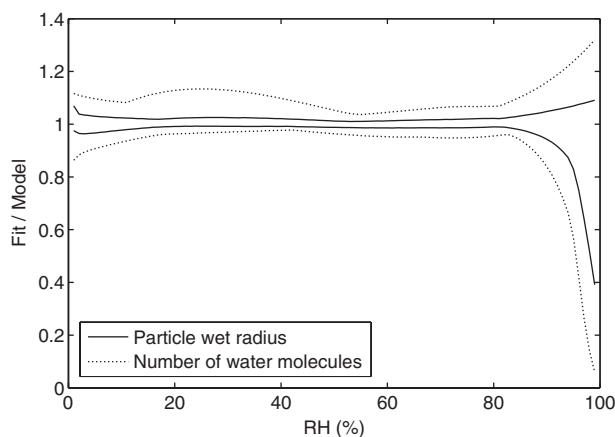

Fig. 1. Ratio of the parameterized and modeled values for the wet radius and the number water molecules as a function of relative humidity in the case of a binary droplet.
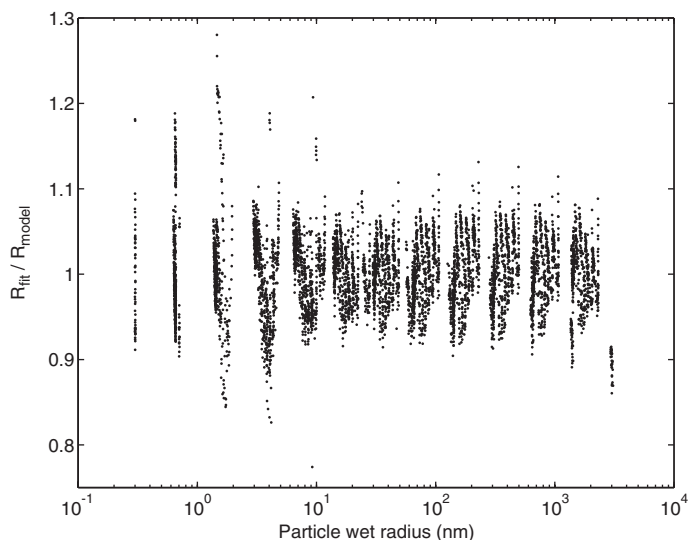
Fig. 2. Ratio of the parameterized and modeled values for the wet radius of the ternary droplet as a function of the wet radius (modeled).

the range 0.67–1.5. The parameterization of ammonia molecules is somewhat less accurate with 55% of the ratios between 0.67 and 1.5. The separated set of points at the top left corner of Fig. 3 is not consequential because the number of ammonia molecules is practically zero. The reason for the relatively inaccurate particle number parameterizations can be traced back to the rather unpredictable behavior of the total number of particles in certain regions of concentration space, most of which is related to the difficulties with the classical droplet model, as mentioned above.

Figs. 4-8 illustrate the droplet radius and molecular content in specific ambient conditions. Fig. 4 shows the radius of the wet particle as a function of relative humidity at $T=280$ K and $\xi=10$ ppt. The number of sulfuric acid molecules is indicated in the figure. Both parameterizations reproduce the model values quite well, only at the highest relative humidities the deviations are significant (cf. Fig. 1). In all cases the ternary droplet is smaller than the binary droplet: the presence of ammonia in the droplets tends to reduce the water content. This difference is most prominent when the
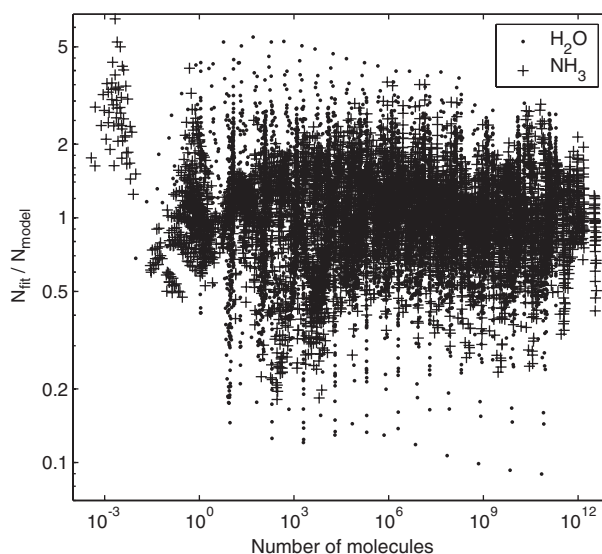

Fig. 3. Ratio of the parameterized and modeled values for the number of sulfuric acid and ammonia molecules in the ternary droplet. The horizontal axis shows the number of acid or ammonia molecules in the droplet (modeled).
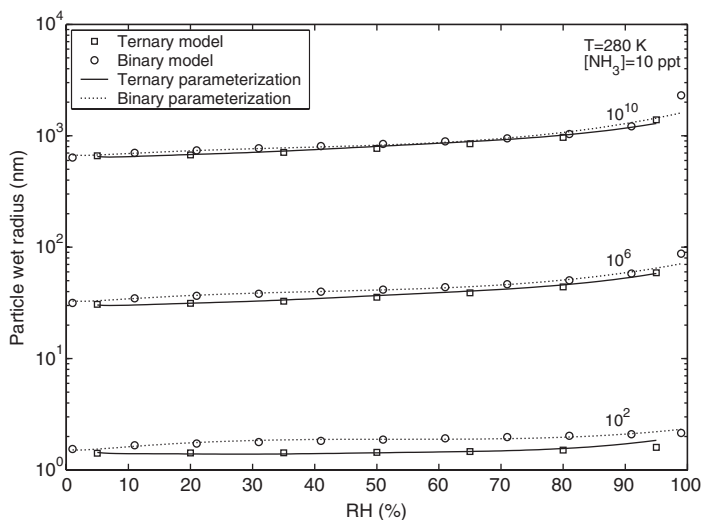
Fig. 4. Wet radius of the particle as a function of relative humidity. The models and the parameterizations are compared at $T=280$ K and $\xi=10$ ppt. The number of sulfuric acid molecules in the droplet is indicated in the figure.

droplet is small; the ternary model produces critical clusters which are almost water-free (Napari et al., 2002b). The radius increases with increasing relative humidity because at high RH the droplet contains more water molecules. The ammonia content in the vapor has little effect on the droplet radius, as shown in Fig. 5 for $T=280$ K, $RH=50\%$, and three values of N_a, although a slightly decreasing trend can be seen with increasing mixing ratio of ammonia. The crosses at the left edge of the figure show the binary limit for the three cases which is in excellent agreement with the ternary model with low ammonia concentrations and parameterizations.

The number of each particle species in the droplet is a linear function of N_a as shown in Fig. 6 at $T=270$ K, $RH=50\%$ and $\xi=31.6$ ppt. However, the water content of the ternary droplets practically disappears if N_a is less than a couple of tens of molecules, whereas even the smallest binary droplets always contain water. Fig. 7 shows the numbers of molecules of each species (binary and ternary) as function of relative humidity when $N_a=10\,000$, $T=280$ K, and $\xi=10$ ppt. The water content increases with relative humidity, as already suggested by Fig. 4. In the ternary case the increase is even more than two orders of magnitude in the range $RH=5$–95%, and

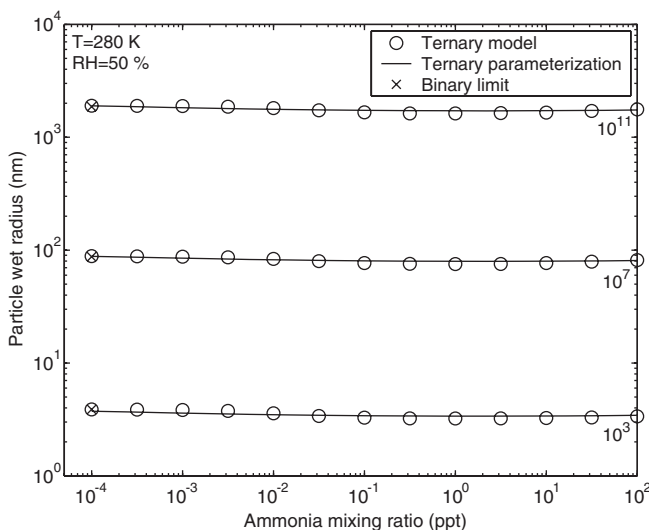

Fig. 5. Particle wet radius as function of ammonia mixing ratio at $T=280$ K and $RH=50\%$. The number of sulfuric acid molecules in the droplet is indicated in the figure.

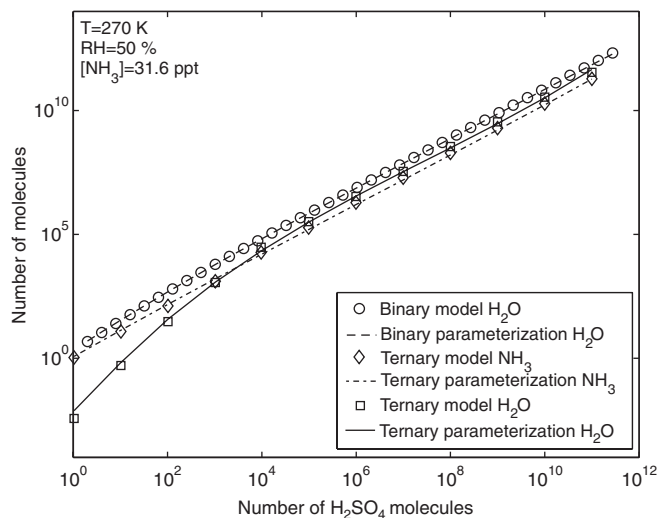*I. Napari et al. / Atmospheric Research 82 (2006) 514–522*

Fig. 6. Number of molecules (water and ammonia) as a function of the number of sulfuric acid molecules. The ambient conditions are indicated in the legend.

the parameterization is able to produce this behavior accurately. Interestingly, the number of ammonia molecules is almost constant. Fig. 8 presents the molecular content as a function of ammonia mixing ratio for $T=280$ K, $RH=50\%$, and $N_a=10^3$; 10^7; 10^{11}. The number of ammonia molecules decreases with decreasing ammonia mixing ratio, but, even at $\xi=10^{-4}$ ppt the droplet still contains some ammonia. On the other hand, the water content is very close to the binary water–sulfuric acid limit at $\xi=10^{-4}$ ppt, indicated by crosses at left-hand border of the plot. The

difference between the binary model and parameterized values is negligible.

Fig. 9 presents the ratio N_b/N_a as a function of the number of sulfuric acid molecules in the droplet for the same values of temperature and relative humidity as Fig. 8, and for various mixing ratios of ammonia. The ratio N_b/N_a is close to 2 when the droplet is large and ammonia mixing ratio high, which indicates that the droplets consist of water and ammonium sulfate. The relative number of ammonia molecules decreases with decreasing ammonia mixing ratio, and for sufficiently
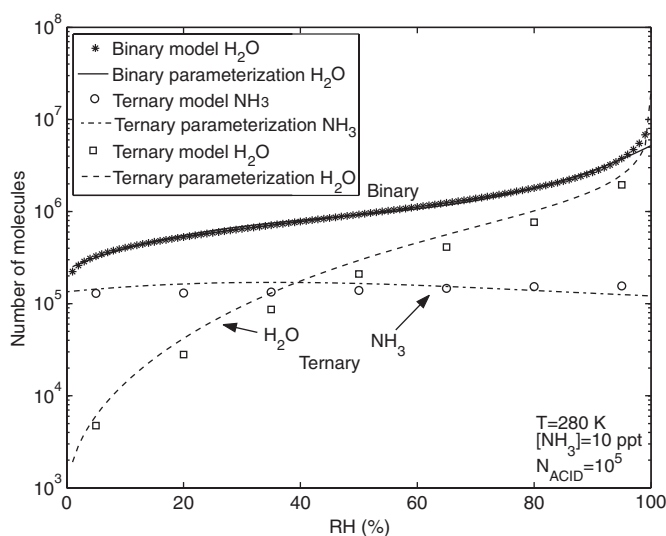

Fig. 7. Number of molecules (water and ammonia) as a function of relative humidity when the droplet contains 10 000 molecules of sulfuric acid. Temperature is 280 K and ammonia mixing ratio 10 ppt.
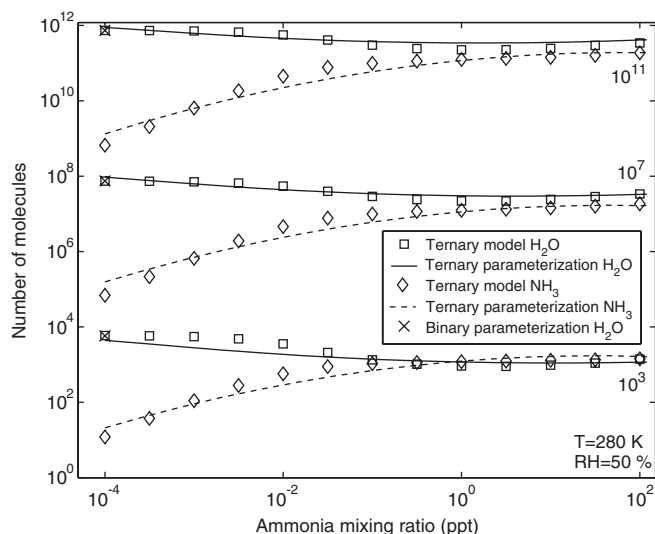
Fig. 8. Number of molecules (water and ammonia) as a function of ammonia mixing ratio. Temperature is 280 K and relative humidity is 50%. Number of sulfuric acid molecules in the droplet is indicated in the legend.

large droplets the ammonia content is independent of droplet size. The very smallest clusters are most probably almost pure ammonium bisulfate, because they have approximately the same number of sulfuric acid and ammonia molecules, and very little water. Because of the problems with the classical droplet model and numerical difficulties, the limit of one sulfuric acid molecule is mostly missing in Fig. 9; it nevertheless seems that the ammonium bisulfate limit is

reached at $N_a = 1$ even at high ammonia mixing ratios. It should be noted that the ratio N_b/N_a is always between 1 and 2, i. e. between pure ammonium bisulfate and pure ammonium sulfate.

5. Conclusions

We have presented parameterizations for binary water–sulfuric acid and ternary water–sulfuric acid–
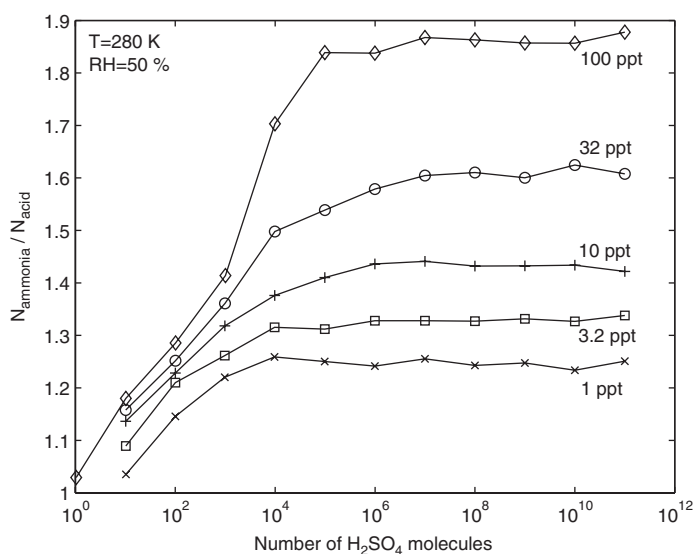

Fig. 9. The ratio of the numbers of ammonia and sulfuric acid molecules in the droplet N_b/N_a as a function of N_a according to the model data. Temperature is 280 K and relative humidity 50%. Ammonia mixing ratio is indicated in the figure.

ammonia droplets suitable for use in atmospheric and aerosol dynamic models.[1] The parameterized properties are particle wet radius and the molecular number of water and ammonia when number of sulfuric molecules in the droplet is given.

The ambient conditions covered by the parameterizations are: temperature 190–330 K (ternary 240–300 K), number of sulfuric acid molecules $2–10^{11}$ ($1–10^{11}$), relative humidity 1–99% (5–95%), and ammonia mixing ratio $10^{-4}–100$ ppt. The parameterizations reproduce the model data with considerable accuracy in most cases, although at relative humidities close to 100% large deviations are expected. We do not recommend using the ternary parameterizations at the binary water–sulfuric acid limit, because in many cases the droplet at ammonia mixing ratio of 10^{-4} ppt still contains ammonia to a large degree. On the other hand, the ternary parameterization can be used, if needed, up to 1000 ppt of ammonia without adverse effects, although there will be some loss of accuracy.

One must bear in mind that the parameterizations can only be as good as the full model, and the validity of the model results depend on the thermodynamic models and the concept of the classical (macroscopic) droplet, the latter of which is not expected to be accurate for the smallest droplets. We also point out that the same thermodynamics and droplet model were used in our nucleation studies of ternary nucleation (Napari et al., 2002b). That work suggested that the nucleating droplet contains both sulfuric acid and ammonia in approximately equal amounts; whether this is the case remains to be seen. However, the classical model is certainly valid for larger droplets, and we are quite confident that the calculated compositions and sizes are close to those actually observed.

Our parameterizations are limited to water–sulfuric acid and water–sulfuric acid–ammonia droplets, although large atmospheric droplets are likely to contain multitude of different chemical species. This is likely to cause further differences between observed and modelled radii. Taking all these chemical compounds into account would be a daunting task and not attempted here, partly owing to the lack of thermodynamic data and models. However, our parameterizations give a reasonable approximation of the properties of wet atmospheric particles, at least beyond nucleation regime, and serve as a benchmark for future work and laboratory measurements.

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[1] Fortran subroutines of the parameterizations are available at http://www.atm.helsinki.fi/~hvehkama/julk.html.

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