

## Simulation of atmospheric nucleation mode: A comparison of nucleation models and size distribution representations

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[1] Atmospheric particle formation and growth were investigated using different nucleation models and size distribution representations. Nucleation was modeled using recently developed parameterizations for binary nucleation of water and sulphuric acid and ternary nucleation of water, sulphuric acid, and ammonia. A comparison with older nucleation parameterizations, combined with full aerosol dynamics, demonstrated that the difference in nucleation rate (1–2 orders of magnitude) is clearly reflected in the resulting total particle concentration. A comparison of binary and ternary nucleation schemes showed that above 240 K the ternary nucleation rate exceeds the binary by over 10 orders of magnitude, indicating that in most cases, at lower tropospheric conditions, only ternary nucleation can be relevant. In addition, the performance of aerosol dynamics models applying either a multimodal monodisperse or a fixed sectional size distribution representation was evaluated against a molecular resolution model, which follows the changes in the nucleation mode particle size distribution molecule by molecule. Regarding total number concentration, the sectional method converged to the molecular resolution approach when increasing the number of size sections. With strong condensational growth, however, numerical diffusion problems were evident. Overall, the performance of the sectional method with low number of sections was not satisfactory. The monodisperse method gave very good results, at least in terms of total number, when the background modes were set to match the condensation sinks of respective lognormal modes. On the basis of our study the multimodal monodisperse method seems to be a possible candidate when selecting the size distribution approach for large-scale atmospheric models. *INDEX*

*TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 3210 Mathematical Geophysics: Modeling; *KEYWORDS:* aerosol modeling, size distribution descriptions, binary nucleation, ternary nucleation

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### 1. Introduction

[2] Since the preindustrial times, human activities have notably elevated the atmospheric concentration of anthropogenic aerosols, mainly composed of sulphate, nitrate, and secondary organics in the submicron range. Several studies have shown that aerosols affect the radiation balance of

Earth's climate [Charlson *et al.*, 1992; Intergovernmental Panel on Climate Change (IPCC), 2001] as well as have effects on acid rain, air quality, and human health [IPCC, 2001; Dockery *et al.*, 1992; Dockery and Pope, 1994]. Recently, research has focused on sulphate aerosols, especially on the smallest particles and their formation processes. Although observations of new particle formation events in the atmosphere are frequent, the microphysical nucleation mechanism has remained unknown. Many studies have suggested the binary nucleation of sulphuric acid and water to be the prevailing mechanism [Doyle, 1961; Raes and Van Dingenen, 1992; Kulmala *et al.*, 1998a], and in some cases

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this theory has successfully explained the observed formation rates of new particles [Weber *et al.*, 1999; Pirjola *et al.*, 1998]. Field studies have shown, however, that experimental nucleation rates frequently exceed those predicted by sulphuric acid-water nucleation theories and laboratory measurements [Weber *et al.*, 1997; Covert *et al.*, 1992; Clarke *et al.*, 1998; Kulmala *et al.*, 1998b; O'Dowd *et al.*, 1999; Birmili *et al.*, 2000; Viisanen *et al.*, 1997]. A possible explanation to the discrepancy is the participation of a third compound to the nucleation process, the most likely species being ammonia ( $\text{NH}_3$ ). Apart from being abundant in the atmosphere, ammonia has the ability to lower the vapor pressure of sulphuric acid above solution surfaces [Marti *et al.*, 1997], thus enhancing the expected nucleation rates by several orders of magnitude compared to  $\text{H}_2\text{SO}_4$ - $\text{H}_2\text{O}$  nucleation alone, as shown by recent theoretical calculations [Coffman and Hegg, 1995; Napari *et al.*, 2002a] and preliminary experimental findings [Ball *et al.*, 1999].

[3] To reconcile theoretical predictions with experimental observations, it is useful to be able to simulate mathematically the dynamic behavior of the aerosol population. In large-scale atmospheric models involving aerosol dynamics, it is necessary to minimize the computer time needed and thus use parameterized nucleation rates. We have therefore recently introduced revised parameterizations for both sulphuric acid-water binary nucleation [Vehkamäki *et al.*, 2002] and sulphuric acid-ammonia-water ternary nucleation [Napari *et al.*, 2002b] with rigorous nucleation kinetics, thermodynamically consistent version of the classical nucleation model, and an improved hydrate model [Noppel *et al.*, 2002]. When compared with our earlier binary parameterization [Kulmala *et al.*, 1998a], the nucleation rates from the revised parameterizations are higher up to several orders of magnitude. In the atmosphere (and in atmospheric models), however, nucleation occurs simultaneously with other dynamical processes such as depletion of nucleating vapors and coagulation loss of newly formed particles. As the differences in observed particle concentration may therefore diverge from those expected on the basis of different nucleation models alone, the models should not be compared in isolation from other aerosol dynamics processes.

[4] In nucleation simulations, another point to bear in mind is that newly formed particles do not have considerable impact on, for example, climate or health before they grow in size. In order to be reliable, the atmospheric model used should mimic accurately not only the formation but also the growth of nucleated particles. Apart from the fairly well-known microphysics of the growth processes, the key factor in the models in this respect is the approach chosen to describe the particle size distribution. Most of the previous studies, which have compared to what extent the chosen particle size distribution approximation affects model predictions, have focused on simulating condensation or coagulation alone [Seigneur *et al.*, 1986; Zhang *et al.*, 1999]. For newly formed particles both condensation and coagulation are likely to be important and the applicability of various approaches cannot be determined solely on the basis of separate comparisons. Studies by Pirjola *et al.* [1999] and by Jacobson [2002] discuss simultaneous simulation of binary nucleation and other major aerosol dynamics processes. While Pirjola *et al.* [1999] compared several distribution representations, their scenarios with condensa-

tional growth rates greatly exceeding the typical measured rates [Birmili and Wiedensohler, 2000; Kulmala *et al.*, 2001] did not represent the most typical atmospheric nucleation events. On the other hand, Jacobson [2002] accounted for nucleation, condensation, coagulation and dissolution/chemistry in his simulations run with moving center method. In a comparison of results from moving center and full moving approaches, however, he neglected coagulation.

[5] The objective of our study is twofold: First, we compare the simulation results given by three nucleation models when combined with full aerosol dynamics. In addition to the revised parameterizations of Vehkamäki *et al.* [2002] and Napari *et al.* [2002b], we chose an earlier binary  $\text{H}_2\text{SO}_4$ - $\text{H}_2\text{O}$  parameterization by Kulmala *et al.* [1998a]. Second, we discuss the accuracy of size distribution approximations commonly used in atmospheric modeling with focus on simulating the formation and growth of nanometer sized particles. We consider nucleation simultaneously with condensation, coagulation and particle dry deposition, and compare the results with a detailed solution.

## 2. Representation of Particle Size Distribution

[6] The approaches used to represent the particle size distribution in atmospheric models differ greatly in computational accuracy and efficiency. Of the current major approaches, which include modal representation [Seigneur *et al.*, 1986; Whitby and McMurry, 1997], fixed sectional representation [Gelbard and Seinfeld, 1980; Raes and Janssens, 1986], and moving sectional representation [Gelbard, 1990; Kim and Seinfeld, 1990], we consider in this study the first two. To ensure their validity, it is necessary to compare the findings with exact solutions. Whereas analytical solutions have been derived for condensation and coagulation alone [Friedlander and Wang, 1966; Gelbard and Seinfeld, 1979; Seinfeld and Pandis, 1998], no such solutions exist for simulating all aerosol dynamical processes simultaneously. Fortunately, even then obtaining highly detailed approximations for comparison is possible.

[7] The formation and growth of nucleation mode particles being our main focus, we chose as our reference such an approximation: a model that describes particles smaller than 10 nm in diameter molecule by molecule [Lehtinen and Kulmala, 2002]. In this region, the approach is free of discretization errors and mimics the dynamics of newly formed particles in great detail. For Aitken and accumulation mode particles, we used a sectional size distribution representation with 27 fixed sections in the size range of 10–700 nm. Lower size resolution in this region should not lead to significant numerical errors as the change in particle volume due to growth processes is much less perceptible than for nanometer sized particles.

[8] Although accurate, the molecular resolution approach, requiring more than ten thousand size sections, is computationally very demanding and therefore not applicable to most atmospheric models. The fixed sectional method, however, has been applied to a wide range of aerosol dynamics problems with considerably fewer sections, typically a few dozen for the whole particle population [e.g., Raes and Van Dingenen, 1992; Brown *et al.*, 1996; Sun and Wexler, 1998; Kulmala *et al.*, 2000]. While the degree of size distribution approximation may not significantly affect

the simulation of particle growth in coagulation dominated cases, it is well-known that the fixed sectional method suffers from numerical diffusion when condensational growth is simulated with too few size sections. It is of interest therefore to assess how much one can compromise on the accuracy of the size distribution description without compromising on the accuracy of the model results. In this study, we employed the fixed sectional model AEROFOR [Pirjola and Kulmala, 1998; Pirjola, 1999], developed to simulate atmospheric sulphuric acid-water particles. In AEROFOR, the calculation of the particle water content is based on equilibrium thermodynamics, which eliminates numerical diffusion associated with water condensation. The calculation of sulphuric acid condensation is, however, subject to discretization errors. To test the extent of these errors, we used several size resolutions.

[9] Since even the fixed sectional model may be too much of a burden in computationally heavy atmospheric applications, modal approaches are customary especially in 3D models. Typically, in this context, the assumed distribution shapes of the modes have been lognormal. Recently, however, modal aerosol dynamics models with monodisperse mode representation have been developed. In this study, we examined the performance of one such code, MONO32 [Pirjola and Kulmala, 2000; Pirjola et al., 2003], in which each particle mode (nucleation, Aitken, accumulation, coarse) is represented by one monodisperse size section. In this method, the size sections move with particle growth and the approach is not therefore subject to numerical diffusion upon condensation. Upon coagulation the mass of the smaller colliding particle is added to the section of the larger particle. Because of sections moving with growth, this method is not well suited for simulating continuous nucleation: as the monodisperse particles of the nucleation mode grow because of condensation and self-coagulation, no section small enough remains for freshly nucleated particles. Placing these particles into the smallest size section with the preexisting ones requires conservation of number and mass, and thus the monodisperse method somewhat underestimates the growth of earlier formed particles. While this simple representation of the size distribution is easy to program and computationally efficient, its approximations are quite rough. One of the main aims of this paper was to validate the monodisperse method against more exact models. In addition, it is of great importance to compare the method with sectional methods with low resolution (i.e., small number of size sections) since these are another strong candidate for large 3D atmospheric models.

[10] All the models used in the study conserve mass and solve for the effect of vapor production, nucleation, and condensation on vapor concentration simultaneously. To obtain a numerical solution to the set of differential equations for gas and particulate phase time evolution, AEROFOR and MONO32 use NAG-library *The Numerical Algorithms Group Ltd.* [1990], whereas the molecular resolution model applies a simple Euler forward time integration scheme.

### 3. Results and Discussion

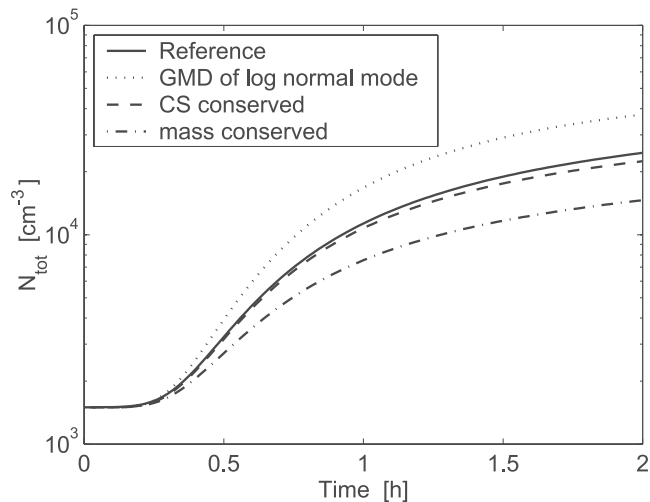
[11] Our primary interest was to study the factors affecting the simulation of atmospheric nucleation mode particles.

In order to be able to compare particle production rates given by several nucleation parameterizations when combined with full aerosol dynamics, and to assess the applicability of a fixed sectional and moving monodisperse size distribution approaches for modeling particle formation and growth, we simulated homogeneous nucleation simultaneously with condensation, coagulation, and particle dry deposition. While focusing on the main characteristics of the size distribution evolution, we made the following simplifying assumptions: Along with water, the only condensable vapor in the simulations was sulphuric acid whose saturation pressure was assumed negligible. While this assumption is well justified for high acid concentrations and particles larger than 10 nm in diameter, it may slightly overestimate the condensational growth of the smallest particles at low vapor concentrations. The source rate for sulphuric acid was constant throughout each simulation. The simulation time of 1–2 hours proved to be adequate to reveal the differences between the nucleation models and size distribution representations. Using a longer timescale, on the other hand, would have complicated the comparison of the performance of size distribution approaches since the newly formed particles would have grown to overlap with the Aitken mode. It is noteworthy, however, that determination of the impact of nucleation on the particle size distribution generally requires a timescale of several hours.

[12] In the molecular resolution and fixed sectional models, the preexisting particle size distribution consisted of two lognormal modes with sulphuric acid particle concentration, dry diameter and standard deviation values  $1200 \text{ cm}^{-3}$ , 20 nm and 1.25 for the Aitken mode, and  $300 \text{ cm}^{-3}$ , 100 nm and 1.3 for the accumulation mode. Such particle size distributions are typical in Boreal forest regions prior to nucleation [e.g., Mäkelä et al., 2000]. The sectional model AEROFOR was run with four size resolutions: 9, 27, 54, and 100 logarithmically spaced sections over the diameter range 0.6–2  $\mu\text{m}$ .

[13] In MONO32, three moving monodisperse size sections represented nucleation, Aitken, and accumulation modes. When determining the initial particle distribution in the monodisperse model, one must note that it is impossible to concurrently conserve number concentration, condensation sink [Kulmala et al., 2001], and mass in conversion from lognormal to monodisperse mode. Choosing to conserve the particle concentrations in the preexisting modes, we compared three approaches to initialize their dry diameters in a 2-hour simulation of ternary nucleation (Figure 1).

[14] Placing the particles at the geometric number mean diameter (GMD) of the lognormal mode overestimates the size of the smallest nucleation mode particles and, on the other hand, underestimates the size of the largest preexisting particles in each mode. The greater the particle size difference, however, the stronger the coagulation loss of the small particles. This way of initialization underestimates also the sulphuric acid condensation rate, which for the small particles is proportional to the particle surface area and in the transitional regime proportional to  $d_p^\lambda$ , where  $1 < \lambda < 2$  and  $d_p$  is the particle diameter. Compared to the reference model therefore this approach predicts an earlier onset of nucleation and a higher concentration of nucleated particles. The opposite is true when the initial diameter in



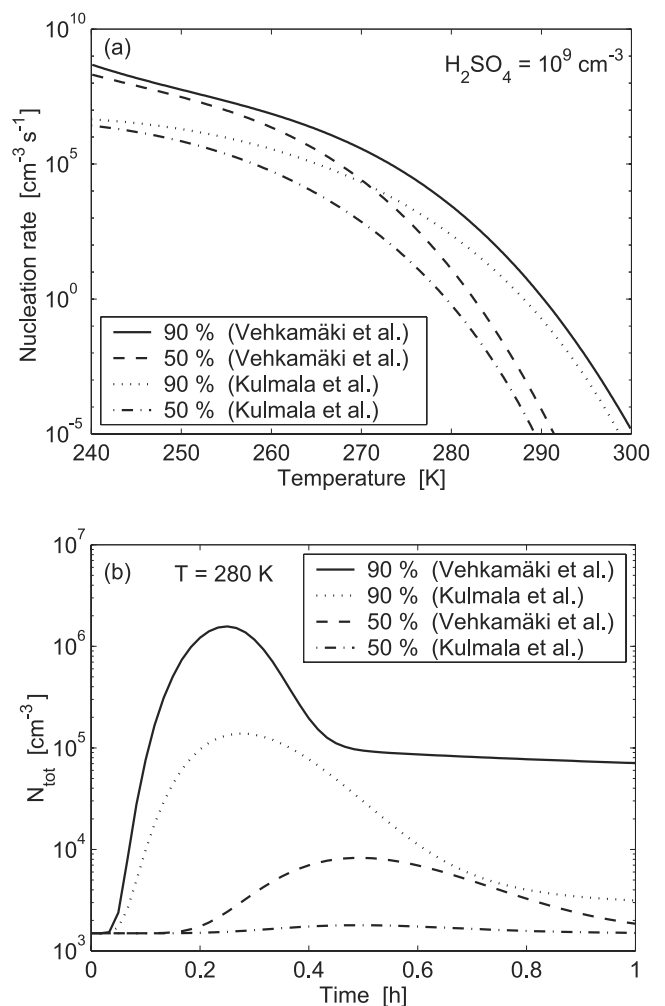
**Figure 1.** Comparison of particle concentration evolution predicted by the molecular resolution model and the monodisperse approach with three methods to initialize the particle size distribution. The locations of the monodisperse modes are determined by placing the particles at the geometric number mean diameter (GMD) of the lognormal mode or by conserving either condensation sink (CS) or mass of each respective mode. See Figure 6 caption for more information on simulation conditions.

MONO32 is determined by matching the particle mass of each lognormal and monodisperse mode at the beginning of the simulation: the underestimation of total particle concentration is due to reduced sulphuric acid concentration as the approach predicts too high a sink for the vapor. The influence of existing particles on nucleation mode evolution stems from the particles acting as a condensation sink for vapor molecules and as coagulation sink for the freshly nucleated particles. As one would expect therefore the choice of initial sizes that matches the condensation sinks of each lognormal and monodisperse mode yields the closest agreement with the molecular resolution model. Thus in the simulations below, we used this approach to determine the dry diameters of the monodisperse modes.

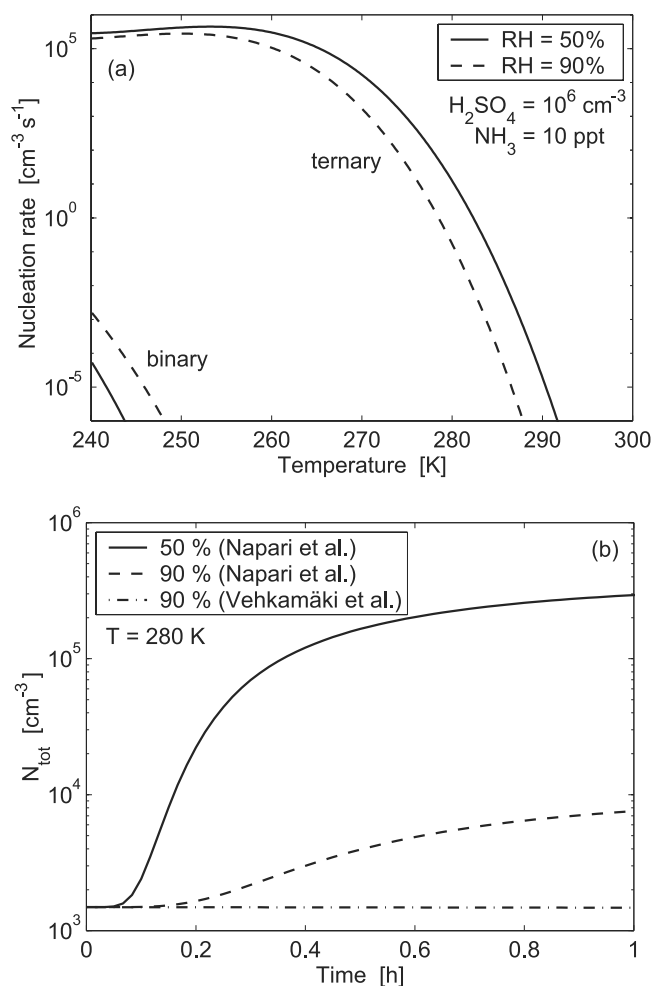
### 3.1. Comparison of Nucleation Models

[15] The nucleation models compared were the ternary parameterization of *Napari et al.* [2002b], and the binary parameterizations of *Kulmala et al.* [1998a] and *Vehkamäki et al.* [2002]. *Noppel et al.* [2002] discuss in detail the differences between the binary models behind the two parameterizations, and conclude that the model behind the *Vehkamäki et al.* parameterization gives somewhat higher nucleation rates than the parameterization of *Kulmala et al.* To enable the comparison with experimental results, they show, however, calculations made only at few temperatures below 240 K and above 295 K, disregarding a wide range of atmospherically relevant conditions. Figure 2a partly fills this gap by substantiating the conclusions of *Noppel et al.* at  $\text{H}_2\text{SO}_4$  concentration  $10^9 \text{ cm}^{-3}$  and a range of temperatures. The nucleation rates given by the two binary parameterizations differ by 1–2 orders of magnitude below 285 K but are within an order of magnitude at temperatures above that.

[16] When nucleation is modelled simultaneously with other aerosol processes, the observed new particle concentration is dependent not only on particle production rate but also on loss processes such as coagulation. In addition, the nucleation precursor vapors are not constant in concentration and we observe, for example, shorter nucleation bursts because of faster depletion of sulphuric acid when the nucleation rate increases. One could therefore expect that the additional dynamics processes may smooth out the effect of the nucleation model. This, however, seems not to be the case as Figure 2b illustrates (see figure caption for detailed information on simulation conditions). When we combine the two binary parameterizations with full aerosol dynamics model, the fixed sectional approach using 27 size sections, the differences in peak and final particle concentrations correlate well with differences in parameterized nucleation rates. One reason for this can be that the high



**Figure 2.** Comparison of binary nucleation parameterizations of *Vehkamäki et al.* [2002] and *Kulmala et al.* [1998a] at relative humidities 50% and 90% in terms of (a) nucleation rate at sulphuric acid concentration  $10^9 \text{ cm}^{-3}$  and (b) time evolution of total particle concentration at 280 K. In Figure 2b the constant sulphuric acid production rates  $3.5 \cdot 10^6 \text{ cm}^{-3} \text{ s}^{-1}$  for RH = 90% and  $1.7 \cdot 10^6 \text{ cm}^{-3} \text{ s}^{-1}$  for RH = 50% lead to a concentration of approximately  $10^9 \text{ cm}^{-3}$  prior to nucleation.



**Figure 3.** Comparison of binary parameterization of Vehkamäki et al. [2002] and ternary parameterization of Napari et al. [2002b] at relative humidities 50% and 90% in terms of (a) nucleation rate at sulphuric acid concentration  $10^6 \text{ cm}^{-3}$  and ammonia mixing ratio 10 ppt and (b) time evolution of total particle concentration at 280 K. In Figure 3b the constant sulphuric acid production rate  $3.5 \cdot 10^3 \text{ cm}^{-3} \text{ s}^{-1}$  leads to a concentration of approximately  $10^6 \text{ cm}^{-3}$  prior to nucleation.

sulphuric acid concentration required for the onset of binary nucleation leads to fast condensational growth of newly formed particles, thus diminishing their coagulational loss.

[17] Apart from, for example, power plant or volcanic plumes where the sulphuric acid concentration may rise very high, atmospheric particle formation by binary  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  mechanism is possible only at very low temperatures (e.g., in the free troposphere) as the sulphuric acid concentrations measured are typically of the order of  $10^5\text{-}10^7 \text{ cm}^{-3}$  [Eisele and Tanner, 1993; Weber et al., 1997]. Such concentrations are, however, sufficient to induce ternary  $\text{H}_2\text{SO}_4\text{-NH}_3\text{-H}_2\text{O}$  particle formation at a range of temperatures, as shown in Figure 3a comparing the binary parameterization of Vehkamäki et al. with the ternary parameterization of Napari et al. in the temperature range for which both of the parameterizations are valid. Although the effect of ammonia drastically decreases at temperatures lower than those shown

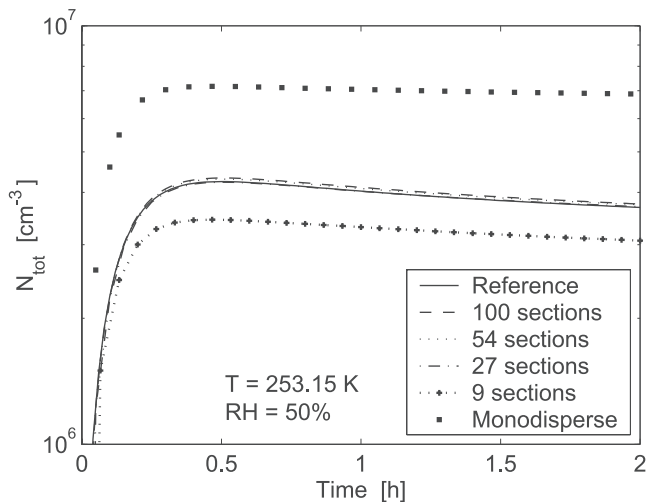
in the figure [Napari et al., 2002a], the nucleation rate from the ternary parameterization exceeds the binary rate by more than 10 orders of magnitude above 240 K. Thus it is obvious that significant ternary nucleation can occur at conditions under which binary mechanism fails to produce new particles (Figure 3b).

### 3.2. Comparison of Size Distribution Representations

[18] In order to assess the accuracy of the fixed sectional and the moving monodisperse models in simulating new particle formation and growth, we evaluated the models against the molecular resolution approach. Pirjola et al. [1999] compared the sectional and monodisperse models used in this work for simulating binary nucleation. As the fundamental equations in these models have not undergone modifications, we refer the reader to their study and focus here on simulating ternary nucleation, highly more relevant of the two particle formation mechanisms at atmospheric conditions. Two test cases were chosen for model evaluation: in the first one the main process causing the growth of newly formed particles was coagulation, whereas in the second case both condensation and coagulation were important. Pirjola et al. [1999] addressed the third possible case, i.e., condensation dominated growth of new particles, in their simulations of binary nucleation, the onset of which requires high sulphuric acid concentration. Since changing the particle formation mechanism to ternary nucleation would not change their conclusions on the performance of the size distribution approaches, we chose not to include a condensation dominated test case. For more detailed information on the simulation conditions of our test cases, see the figure captions.

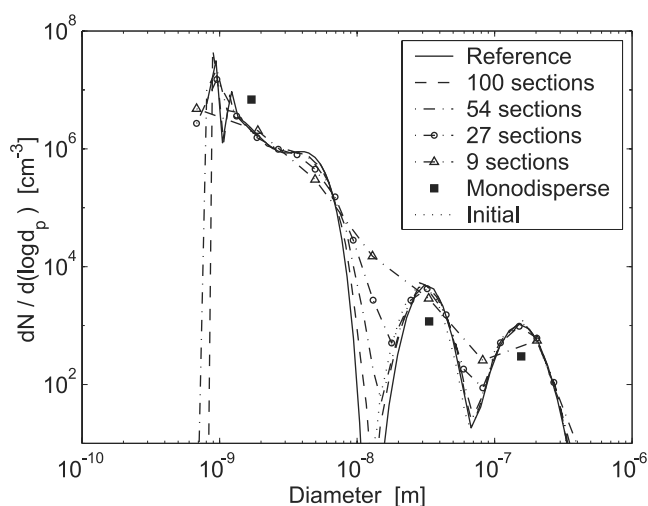
[19] In the first test case, the highly elevated nucleation mode particle concentration of the order of  $4 \cdot 10^6 \text{ cm}^{-3}$  leads to strong self-coagulation. This effect dominates over condensational growth of the nucleation mode, particularly as the formation of new particles reduces the condensable sulphuric acid concentration to little over  $10^5 \text{ cm}^{-3}$ . Figures 4 and 5 show the performance of the size distribution representations at these conditions. The total particle concentration given by the fixed sectional approach, known to simulate coagulation fairly accurately, agrees well with the molecular resolution approach; only the lowest size resolution of 9 sections notably underestimates the particle concentration after a 2-hour simulation but results in an error of less than 20% (Figure 4). Conversely, the monodisperse approach overestimates the nucleation mode particle concentration by almost 90%. This is mainly due to the inability of the highly simplified approach with only three monodisperse modes to account for the total coagulational loss of newly formed particles.

[20] Figure 5 displays the final particle size distribution after 2 hours for the same test case. Note that in the figure the particle number concentration on the vertical axis is plotted as  $dN/d(\log_{10}d_p)$  for the molecular and the fixed sectional models and as total particle concentration  $N$  for the monodisperse model, and therefore the monodisperse particle mode peak heights are not directly comparable to those given by the other models. The fixed sectional approach with 100 size sections agrees very well with the reference model for particles with diameters above 20 nm and captures the growth of the nucleation mode accurately



**Figure 4.** Comparison of molecular resolution, fixed sectional, and moving monodisperse models in terms of time evolution of the total particle concentration at 253.15 K and relative humidity 50%. Ammonia mixing ratio is 10 ppt, and sulphuric acid has a constant production rate  $2.1 \cdot 10^4 \text{ cm}^{-3} \text{ s}^{-1}$ .

aside from slight numerical diffusion spreading out the mode. Both the reference simulation and the fixed sectional simulation with 100 sections show a drop and an increase in particle concentration for very small particles. This fluctuation at the fine size resolutions is due to the fact that when two freshly nucleated particles collide, the forming new particle is so large in size that it is not placed to the size section right next to that of freshly formed particles. This skipped particle section is not, however, empty since, although self-coagulation dominates their growth, the small particles grow also by condensation.

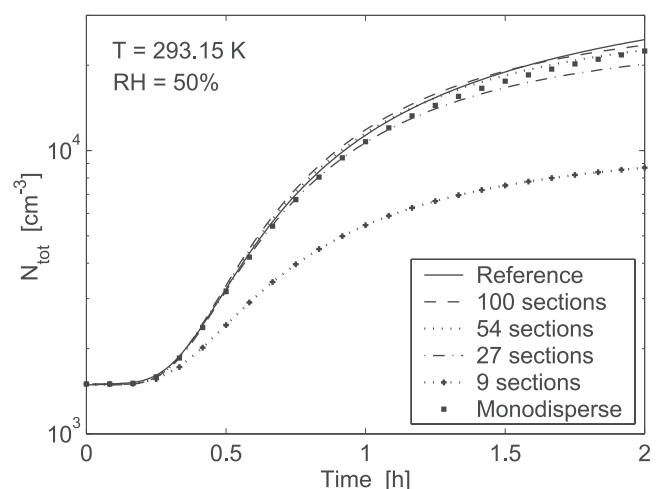


**Figure 5.** Comparison of molecular resolution, fixed sectional, and moving monodisperse models in terms of final particle size distribution after a 2-hour simulation. For the monodisperse model, y axis values indicate the total concentration in each respective particle mode. Simulation conditions as in Figure 4.

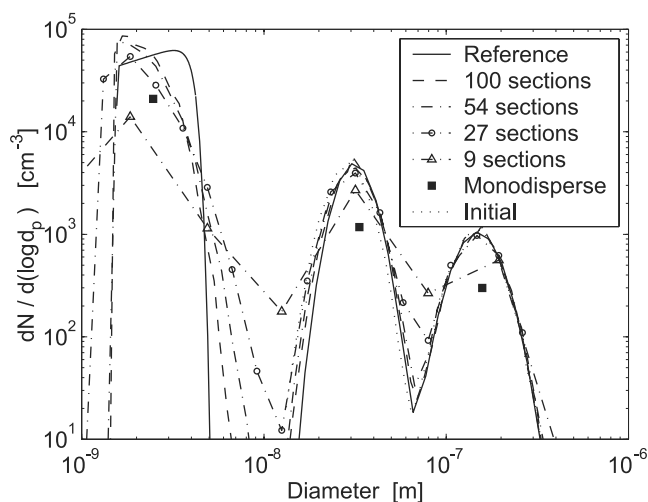
[21] For lower size resolutions in the fixed sectional model, the discretization errors are much more pronounced leading to severe overprediction of the growth of nucleated particles and noticeable numerical diffusion also in the Aitken mode. In addition, with 9 size sections the approach fails to reproduce three distinct particle modes altogether. Some improved versions of the fixed sectional method exist, in which less numerical diffusion with pure condensational growth has been observed: for example, Bott's method [Meng *et al.*, 1998], the spline method by Lurmann *et al.* [1997], the moving center method by Jacobson [1997] and QSTSE by Nguyen and Dabdub [2001]. The effect of number of sections on the amount of numerical diffusion is, however, qualitatively the same as in the method presented here.

[22] In the monodisperse model, only one particle size represents each mode and the assessment of the applicability of the model for simulating size distribution evolution has to be based on how well the approach predicts the mode average sizes. In our coagulation driven case, the slow growth of Aitken and accumulation particles enables the monodisperse approach to predict their average sizes accurately. Because of the severe overestimation of the concentration of nucleated particles, the approach predicts slightly lower average particle size than the detailed model in the nucleation mode, in which new particle formation pulls the moving monodisperse mode toward smaller particle size and growth of existing particles toward larger particle size.

[23] In the second test case, the nucleation rate is substantially lower leading to new particle concentration of the order of  $2 \cdot 10^4 \text{ cm}^{-3}$ . Because the depletion of sulphuric acid due to particle formation is relatively slow, the acid concentration rises to approximately  $10^7 \text{ cm}^{-3}$  making condensation an important growth process for the nucleation mode. As expected, of the two simulation cases this one proves to be more stringent test for the fixed sectional model. Whereas the approach captures the time development of particle



**Figure 6.** Comparison of molecular resolution, fixed sectional, and moving monodisperse models in terms of time evolution of the total particle concentration at 293.15 K and relative humidity 50%. Ammonia mixing ratio is 10 ppt, and sulphuric acid has a constant production rate  $1.6 \cdot 10^4 \text{ cm}^{-3} \text{ s}^{-1}$ .



**Figure 7.** Comparison of molecular resolution, fixed sectional, and moving monodisperse models in terms of final particle size distribution after a 2-hour simulation. For the monodisperse model, y axis values indicate the total concentration in each respective particle mode. Simulation conditions as in Figure 6.

concentration well with the two finest size resolutions when compared with the reference model, the simulation results with an error of 18% with 27 size sections and 65% with 9 size sections cannot be considered satisfactory (Figure 6). On the other hand, the accuracy of the highly simplified monodisperse model is comparable to that of the sectional model with 54 sections: the approach underestimates the final particle concentration by less than 9%.

[24] The explanation for the poor performance of the fixed sectional approach lies in numerical diffusion: even with the finest size resolution, the discretization errors distort the shape of the nucleation mode and spread out both nucleation and Aitken modes (Figure 7). This increases the condensation sink for condensable vapors and lowers the sulphuric acid concentration available for new particle formation. Although in this case the sectional approach with 9 size sections is capable of reproducing three distinct modes, the mode peak heights are considerably lower and correspondingly the modes wider than with the other size resolutions. On the other hand, the monodisperse model predicts the average size of the nucleation mode well.

#### 4. Conclusions

[25] Atmospheric nucleation mode particle formation and growth have been investigated using different nucleation models and size distribution representations. In the simulated case studies, sulphuric acid vapor with a constant source rate transformed into particles through either a binary nucleation mechanism together with water, or a ternary nucleation mechanism together with water and ammonia. The nucleation process was modeled using recently developed parameterizations for the nucleation rate, and critical particle size and composition. Different nucleation pathways were compared with each other linked with full aerosol dynamics, i.e., condensation, coagulation, and particle dry deposition. Furthermore, the most recent nucleation parameterizations,

based on most rigorous kinetics and consistent thermodynamics, were compared with older ones.

[26] In comparison with older parameterizations, the nucleation rates given by the revised binary scheme were higher by roughly 1–2 orders of magnitude. Other aerosol dynamics processes did not smooth out this difference as much as one might expect: the resulting total particle concentration clearly reflected the difference in nucleation rates. A comparison of binary and ternary schemes showed that above 240 K the ternary nucleation rate exceeds the binary one by over 10 orders of magnitude. Thus, of the two studied mechanisms, only ternary nucleation can be relevant at most lower tropospheric conditions. The occurrence of binary nucleation in, for example, power plant or volcanic plumes, and at very low temperatures in the upper troposphere cannot, however, be ruled out.

[27] In addition to comparing nucleation mechanisms, we evaluated the performance of fixed sectional and multimodal monodisperse size distribution representations in simulating the growth of nucleated particles with the ternary scheme. Although widely used in 3D atmospheric models, this study did not include a modal lognormal approach. As a reference model, we chose a molecular resolution distribution representation, which should in principle be free of discretization errors, such as numerical diffusion. In the multimodal monodisperse method, several intuitively reasonable ways exist to select the representation of the background aerosol. In this study, we set the location of the preexisting modes in three ways: 1) at the number geometric mean diameter, 2) at diameter corresponding to the mean volume, and 3) at the diameter corresponding to the mean condensational sink. The results using the last choice matched the molecular resolution results very well, since the primary factors determining the evolution of the nucleation mode particle concentration are the nucleation rate and the coagulation sink, i.e., coagulation loss onto larger particles.

[28] The model comparison results indicated that regarding total number concentration, the sectional method converges to the molecular resolution approach when increasing the number of size sections. In cases for which condensation along with coagulation was an important particle growth mechanism, however, the sectional simulation with even as many as 100 size sections showed clear artificial smoothing in the nucleation mode size distribution, resulting from numerical diffusion. The overall performance of the sectional method with the lowest size resolution (9 sections) was not very good.

[29] The main practical result of this paper was the finding that the multimodal monodisperse method predicted both the particle number concentration and the particle size distribution much better than the sectional method with low size resolution. This makes the monodisperse method a possible candidate when selecting the size distribution representation for the large-scale atmospheric modes, in which minimizing computational burden of all the subprocesses is important.

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