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MODEL STUDIES ON THE SIZE DISTRIBUTION DYNAMICS OF ATMOSPHERIC AEROSOLS

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Academic dissertation

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Model studies on the size distribution dynamics of atmospheric aerosols

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Abstract

Understanding the dynamic processes shaping the atmospheric aerosol particle size distribution is essential in order to evaluate the effect of the particles on environmental issues such as climate change, and human health. This thesis employs process-oriented aerosol models to investigate the formation and growth mechanisms of atmospheric nanosized particles.

Model studies suggest that atmospherically relevant concentrations of low volatile organic vapours can grow nucleation mode particles to cloud condensation nuclei sizes. Furthermore, such organic compounds may under certain conditions dominate the composition of 3-4 nm particles initially formed from inorganic vapours. In addition, heterogeneous nucleation of sulphuric acid, ammonia and water offers a possible explanation to the patchy sulphate coating observed on atmospheric mineral dust. Although simulations indicate that the sulphate-coated mineral dust particles typically cannot inhibit new particle formation in the atmosphere altogether, dust particles can provide large coagulation sinks for newly formed clusters and thus supress the formation new detectable particles.

In large scale atmospheric models, it is vital to minimize the computational burden of the numerical description of the aerosol size distribution while maintaining the reliability of the model predictions. With the size resolution typical to large scale applications, discretizing the particles into fixed size sections based on their involatile core volume instead of their total volume does not improve the model performance sufficiently. Abandoning the fixed section locations eliminates much of the artificial widening of the size distribution but may introduce additional problems. The moving center method, which lets the particle size vary within the section boundaries, and the retracking method, which lets the size sections move in time but retracks them into a fixed grid after certain time intervals, both predict burst-like rather than continuous formation of detectable particles. The former of the methods may also predict extra dents in the distribution thus distorting its shape. On the other hand, the performance of the simple multimodal monodisperse model in new particle formation simulations can be greatly improved by basing the choice of the pre-existing particle mode locations on the condensation sink of the particle population.

Keywords: Atmospheric aerosols, numerical modelling, particle formation and growth, size distribution representation

Contents

List of publications

This thesis consists of an introductory review, followed by five research articles. Papers are reproduced with the kind permission of the journals concerned.

I Pirjola, L., H. Korhonen, and M. Kulmala, Condensation/evaporation of insoluble organic vapor as functions of source rate and saturation vapor pressure, *J. Geophys. Res.*, 107 (D11), 4108, 10.1029/2001JD001228, 2002.

II Korhonen, H., I. Napari, C. Timmreck, H. Vehkamäki, L. Pirjola, K.E.J. Lehtinen, A. Lauri, and M. Kulmala, Heterogeneous nucleation as a potential sulphate coating mechanism of atmospheric mineral dust particles and implications of coated dust on new particle formation, *J. Geophys. Res.*, 108 (D17), 4546, 10.1029/2003JD003553, 2003.

III Korhonen, H., K.E.J. Lehtinen, L. Pirjola, I. Napari, H. Vehkamäki, M. Noppel, and M. Kulmala, Simulation of atmospheric nucleation mode: A comparison of nucleation models and size distribution descriptions, *J. Geophys. Res.*, 108 (D15), 4471, 10.1029/2002JD003305, 2003.

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1 Introduction

Atmospheric aerosol is a complex mixture of air with liquid and solid phase particles. The origin and the formation mechanism of the particles dictate much of their initial properties; yet, the particles are constantly under the influence of numerous chemical and physical processes that shape their size and composition distributions. This thesis documents the development of numerical process-oriented aerosol models and their application to a variety of atmospheric conditions in order to investigate the dynamics of the particle size distribution evolution.

The motivation behind atmospheric aerosol research lies in the diverse environmental effects of the particles: Areas under the influence of urban or industrial pollution frequently experience visibility degradation due to the ability of aerosol particles to scatter and absorb visible solar radiation [*Chan et al.*, 1999; *Hand et al.*, 2002]. For the same reason, particles forming haze influence the amount of photosynthetically active radiation that reaches the Earth's surface and may thus reduce crop yields by as much as 30% [*Chameides et al.*, 1999; *Bergin et al.*, 2001]. In addition, wet and dry deposition mechanisms bring to the ground acidic particles that disturb soil and fresh water habitats and cause damage to plants and building materials [*Seinfeld and Pandis*, 1998]. Aerosol particles alter also the concentration of important atmospheric oxidants and pollutants by offering surfaces for heterogeneous chemical reactions [*Dentener and Crutzen*, 1993; *Andreae and Crutzen*, 1997; *Meilinger et al.*, 2001; *Tie et al.*, 2001]. Over the polar regions, heterogeneous reactions of chloride and nitrate compounds on polar stratospheric cloud particles are responsible for the observed depletion of the ozone layer [*Brasseur et al.*, 1990; *Hofmann et al.*, 1992].

In recent years, much scientific research has focused on the effects of atmospheric particles on climate change. Aerosol particles can scatter and absorb incoming solar radiation as well as the outgoing thermal radiation, and thus disturb the Earth's radiative balance directly. The indirect climate forcing of the particles through the formation of clouds is usually split into two effects [*Intergovernmental Panel on Climate Change (IPCC)*, 2001]: the first indirect effect, whereby higher aerosol concentrations lead to more cloud droplet activation but, at the same time, to smaller droplets, and the second indirect effect, whereby smaller cloud droplets alter the cloud life time. Besides their size and concentration, the most crucial particle property determining the magnitude and the sign of their climate effects is their composition. Sulphate aerosol,

a major contributor to atmospheric particle load, has long been the main focus of the research on particulate climate effect, and current estimates of its direct and total indirect global forcing range from - 0.2 to - 0.8 W/m² [*Graf et al.*, 1997; *Haywood and Ramaswamy*, 1998; *Myhre et al.*, 1998; *Ghan et al.*, 2001; *Koch*, 2001], and from 0 to -3.2 W/m² [*Lohmann et al.*, 2000; *Ghan et al.*, 2001; *Kristjánsson*, 2002], respectively. Recently, however, the improved understanding of the radiative properties of carbonaceous aerosol constituents has suggested that their climate forcing may be comparable to that of sulphate particles in magnitude [*Hobbs et al.*, 1997; *Hansen et al.*, 1998; *Lohmann et al.*, 2000]. Few estimates of the forcing potential of other particulate components, such as nitrates [*Adams et al.*, 2001] and mineral dust [*Tegen et al.*, 1996; *Hansen et al.*, 1998], are also available but suffer from a high level of uncertainty [*Intergovernmental Panel on Climate Change (IPCC)*, 2001].

In addition to climate studies, another area of intensive aerosol research is their effects on public health. Aerosol particles are, along with ozone, nitrogen oxides and volatile organic compounds, a major component in photochemical smogs, and epidemiological studies have shown a clear linkage between the urban particulate load and human health effects such as an increased risk of severe asthma attacks in children [*Slaughter et al.*, 2003], and excess mortality of infants and the elderly [*Borja-Aburto et al.*, 1998; *Goldberg et al.*, 2001]. Recent studies on animal and human subjects have revealed that inhaled ultrafine particles may pass from the lungs into systemic circulation [*Takenaka et al.*, 2001; *Nemmar et al.*, 2002], which could explain the excess mortality from cardiovascular diseases during air pollution episodes. Despite the well established relation between elevated particulate pollution levels and human health effects, the knowledge on particle properties responsible for the observed symptoms is deficient: different studies have stressed the importance of ultrafine particle concentration [*Seaton et al.*, 1995; *Peters et al.*, 1997], particle surface area [*Brown et al.*, 2001; *Maynard and Maynard*, 2002], or surface composition [*Obot et al.*, 2002].

Full understanding of the complex interactions behind the aerosol environmental effects requires a multidisciplinary approach involving both experimental and theoretical methods. Furthermore, numerical process-oriented models provide a valuable link between field measurements, laboratory studies and theoretical constructs by offering a tool to test hypotheses against experimental data. Ideally, the models should describe the aerosol microphysical processes in detail while also accounting for the related atmospheric chemistry and three dimensional mixing phenomena as realistically as possible.

Unfortunately, the computational requirements for such models exceed the computing power typically available, and thus the 3D chemistry and physics models on global and regional scales need to resort to highly simplified presentation of atmospheric processes. A computationally viable exploration of detailed aerosol microphysics necessitates therefore abandoning the 3D construct and turning to process-oriented box models. Although neglecting the mixing phenomena, box models often provide a sufficient description of the ambient atmosphere. They are therefore valuable in explaining observed aerosol behaviour, answering existing or generating new theoretical questions, and providing insight to mechanisms not accessible with the current experimental instrumentation. Furthermore, box models can act as a testing ground when comparing simplified aerosol representations suitable for large scale models.

This thesis utilizes several microphysical aerosol box models to investigate the dynamic processes affecting fine atmospheric particles. The special focus of the work is on modelling the appearance and subsequent growth of new nanosized clusters. While observations of such particle formation events are frequent all around the world [*Kulmala et al.*, 2003b], the microphysical processes and the gas-phase compounds responsible for the phenomena still suffer from grave uncertainties. Moreover, since the smallest particles contribute very little to the atmospheric particulate mass, many large scale models ignore them altogether. Accurate description of the newly formed particles is, however, essential in order to predict the concentration and appearance rate of inhalable and climatically active particles correctly.

The main objectives of the thesis are to

- study the role of organic vapours in the nucleation mode particle growth [**Papers I and V**]

- investigate the mechanism responsible for the soluble coating of atmospheric mineral particles and the role of such particles in new particle formation [**Paper II**]

- determine how accurately numerical size distribution representations, which are computationally viable for inclusion into large scale atmospheric models, describe new particle formation and growth [**Papers III-V**]

- develop a computationally efficient multicomponent aerosol dynamics model which applies the knowledge gained from the objectives listed above and combines the most recent knowledge on the atmospheric new particle formation [**Paper V**].

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The following section describes the main dynamic processes affecting the atmospheric particle size distribution and lists some of the difficulties encountered when including them into atmospheric models. Section 3 summarizes the most common approaches to solve the size distribution evolution in numerical models and discusses their applicability to describe aerosol dynamics, and especially new particle formation and growth, in large scale models. Section 4 shortly describes the aerosol dynamic models used in this study, and section 5 presents their application to atmospheric studies as it reviews the papers included in this thesis. Finally, section 6 summarizes the main conclusions of the research done.

2 Aerosol dynamic processes in the atmosphere

The subsections below summarize the most important dynamic processes that affect the atmospheric aerosol size distribution. Although not included in the discussion, chemical reactions in the gas phase (influencing the concentrations of nucleating and condensing vapours) and in the particle phase as well as in cloud and fog droplets (changing the particle composition) play also a role in shaping the particle properties. The focus here is on describing the main aerosol particle formation, growth and loss mechanisms, and on discussing the main challenges in incorporating them into aerosol dynamic models.

2.1 Particle sources

Masswise, the most important source of new atmospheric particles is direct natural emissions. Globally, the two main mechanisms, accounting for 80 - 90% of the total new particulate mass [*Seinfeld and Pandis*, 1998; *Intergovernmental Panel on Climate Change (IPCC)*, 2001], are wave breaking or bubble bursting over the oceans, which releases particles consisting mainly of sodium and chloride, and wind blown mineral dust from deserts and other arid areas. Dust particles, whose influence on aerosol dynamics is studied in **Paper II**, are a mixture of various minerals, their composition determined mainly by their origin, and the chemical and physical processes attacking them during their atmospheric transport. Although especially dust is frequently observed several thousand kilometers downwind from its source areas [*Schütz et al.*, 1981;

Prospero, 1999], the natural aerosol particle load typically concentrates close to ocean and desert areas. On spatially or temporally limited scales also biogenic emissions of e.g. leaf wax, viruses and pollen, and volcanic emissions of sulphate particles can contribute significantly to the atmospheric particle mass. On the other hand, anthropogenic sources like biomass and fossil fuel burning, which release mainly soot and organic particles, and handling or storing materials for industrial purposes can emit high local concentrations of inhalable particles and hence cause considerable public health effects. In addition, human activities have reduced vegetation and disturbed soil surfaces, and thus enhanced mineral aerosol production. Technically, the inclusion of natural and anthropogenic particle emissions in a numerical model is fairly straightforward; the main challenges lie in the lack of detailed and source area specific data on particle emission rates and size distributions.

Numberwise an important source of new atmospheric particles is the formation of stable nanosized clusters from gas-phase species. New particle formation via this mechanism is frequently observed in the atmosphere at locations ranging from free troposphere [*Clarke et al.*, 1999; *Twohy et al.*, 2002] to marine and continental boundary layer [*Mäkelä et al.*, 1997; *Birmili and Wiedensohler*, 2000; *O'Dowd et al.*, 1998], and from clean Arctic and Antarctic areas [*Davison et al.*, 1996; *Wiedensohler et al.*, 1996] to polluted urban metropolises [*Williams et al.*, 2000; *Woo et al.*, 2001]. The suggested pathways for the phenomenon are many: The conucleation of sulphuric acid and water to neutral clusters [*Raes and Van Dingenen*, 1992; *Weber et al.*, 1999], a scheme recently complemented with ammonia [*Ball et al.*, 1999; *Kulmala et al.*, 2000], has reached most attention, mainly because of the very low saturation vapour pressure of sulphuric acid and its abundance in the atmospheric gas and particulate phases. Moreover, recent simultaneous measurements of particle size distribution and gas-phase concentrations have supported the idea of sulphuric acid participating in new particle formation [*Weber et al.*, 1997; *Birmili et al.*, 2000], although some theoretical work suggests that the mechanism could be ion mediated nucleation [*Yu and Turco*, 2000; *Lee et al.*, 2003], or kinetically limited nucleation [*Lushnikov and Kulmala*, 1998] rather than homogeneous nucleation of neutral clusters. On the other hand, *Bonn and Moortgat* [2003] have recently proposed that nucleating species in forested areas could be thus far unidentified low volatile organic compounds formed via oxidation of biogenic vapours.

The current instrumentation for aerosol size distribution measurements cannot detect the existence of particles smaller than 3 nm in diameter, and furthermore, no direct

technique exists to determine the composition of nucleation mode particles reliably. It is therefore impossible to verify the triggering mechanism of atmospheric nanoparticle formation experimentally. Detailed process-oriented models offer, however, a helpful tool to bridge the gap between the measurements and the predictions of nucleation theories. **Paper III** demonstrates, for instance, that new particle formation in the troposphere frequently occurs at many orders of magnitude lower sulphuric acid super-saturations than predicted by the classical formulation of binary H_2SO_4-H_2O nucleation theory.

The main challenge in incorporating nanocluster formation in aerosol dynamic models is that the full nucleation models typically require computationally heavy thermo-dynamic calculations. Fortunately, for most modelling applications any information beyond the forming particle size, composition and production rate is unnecessary, and therefore, sufficient information can be obtained from nucleation parameterizations based on detailed thermodynamic models [*Fitzgerald et al.*, 1998; *Pandis et al.*, 1994] or on observations [*Harrington and Kreidenweis*, 1998]. Parameterizations available predict, however, very different nucleation rates [*Zhang et al.*, 1999], and the choice of the parameterization can influence the model results significantly [**Paper III**]. The process models used in this work apply recently revised, thermodynamically consistent nucleation parameterizations for binary sulphuric acid - water [*Vehkamäki et al.*, 2002] and ternary sulphuric acid - ammonia - water nucleation [*Napari et al.*, 2002].

2.2   Particle growth by condensation

The main process responsible for atmospheric particle growth is condensation, in which diffusion transports gaseous molecules onto the particle surface that absorbs and in-corporates them into the particulate matter. If the particle surface cannot absorb the vapour molecule, which might be the case for example for solid particles like mineral dust, the onset of condensation may require heterogeneous nucleation i.e. formation of liquid embryos on the particle surface [**Paper II**]. In addition to contributing to atmospheric particle growth, condensation may under some conditions limit the for-mation, or at least the detection, of new nanosized clusters [**Papers II and IV**]. The pre-existing particles provide a sink for the nucleating vapours, lowering their super-saturation, and may thus hinder new particle formation. Observations in boreal forest regions support this reasoning as they suggest that the condensation and coagulation

sink values show a notable drop during nucleation events [*Dal Maso et al.*, 2002].

The vapour pressure gradient being the driving force of the condensational mass transport, the most important property of gas phase compounds, regarding their uptake into the particles, is their saturation vapour pressure. In the atmosphere, the majority of condensable low or semivolatile vapours forms by oxidation of gaseous emissions from natural and anthropogenic sources. Of the anthropogenic activities, fossil fuel and biomass burning along with industrial activities are the biggest sources of secondary sulphate, nitrate and organic particles, whereas ammonia is mainly released from agriculture. On the other hand, natural sources like oceans and volcanic activity emit sulphur-containing compounds, and vegetation is an important source of volatile organic compounds (VOC). In forested areas, the oxidation products of biogenic VOCs are speculated to be the main contributors to new particle growth [*Kavouras et al.*, 1998]. Model studies have indicated that, in order to explain the observed nucleation mode growth rates, the unidentified condensable organic compounds should have saturation vapour densities of the order of, or lower than 10^6 cm^{-3} [*Kulmala et al.*, 1998; *Kerminen et al.*, 2000; **Paper I**]. Moreover, **Paper V** suggests that such low volatile compounds can dominate the nanocluster composition even at particle sizes below 5 nm in diameter.

When treating the mass transport from gas phase to the particles in atmospheric models, one often has to compromise on accuracy in the favour of model efficiency. Although the dynamic treatment of the mass flux yields the most rigorous results, it is computationally quite heavy especially for large scale atmospheric models. Such models have therefore often assumed that an equilibrium forms between the particulate and gas phases under time scales shorter than a typical model time step [*Binkowski and Shankar*, 1995; *Lurmann et al.*, 1997]. In reality, this assumption is not valid under all conditions or for all condensable vapours [*Allen et al.*, 1989; *Harrison and MacKenzie*, 1990; *Meng and Seinfeld*, 1996]. It is therefore accustomary to combine the two approaches and assume equilibrium only for some compounds while treating condensation dynamically for others. This approach is used in all the models applied in this study: **Papers I-IV** assume instanteneous equilibrium of aerosol particles with water, and **Paper V** with water and ammonia.

Wexler and Seinfeld [1990] have pointed out that even if the aerosol is in equilibrium with the gas phase species, distributing the condensing compound to the particles based solely on thermodynamic considerations may not give correct results. Motivated by this

finding, *Pandis et al.* [1993] developed a scheme which establishes equilibrium with the whole modelled aerosol population but partitions the condensing mass among the size sections based on mass transport considerations. In reality, the equilibrium assumption is often valid for fine particles but may lead to serious errors when applied to the coarse mode particles that typically take several hours to establish equilibrium [*Meng and Seinfeld*, 1996]. To correct the mass transport to these large particles, *Capaldo et al.* [2000] have suggested a method that combines the dynamic and equilibrium approaches: it establishes an equilibrium for particles smaller than a chosen threshold diameter, typically 1 μm, and solves the mass transport dynamically for larger particles. Model comparisons have shown that this combined method reproduces dynamic results fairly well at considerably lower computational cost [*Capaldo et al.*, 2000; *Koo et al.*, 2003], encouraging its implementation into 3D atmospheric models [*Gaydos et al.*, 2003].

2.3   Particle loss

Collisions of aerosol particles with each other reduce their number concentration but conserve total particulate mass. Atmospheric particles can collide as a result of many different processes such as velocity gradients produced by turbulent flows, differences in gravitational settling velocities, and external force fields [*Seinfeld and Pandis*, 1998]. For fine particles, the most important mechanism bringing them together is, however, Brownian motion. The collision efficiency due to Brownian motion rises quickly with the difference in particle size; the smallest particles move about rapidly and hit most easily the particles providing the largest target area. Coagulation lowers therefore most efficiently the concentration of the smallest atmospheric particles and may even remove the freshly nucleated particles before they reach detectable sizes [*Kerminen et al.*, 2001; **PaperII**]. On the other hand, if the concentration of newly formed particles is sufficiently high, of the order of 10^7 cm^{-3}, their self-coagulation may provide an important mechanism for their initial growth [**Paper II**].

Numerical modelling of particle coagulation can consume lot of computer time compared to other aerosol dynamic processes, and some models have, therefore, neglected the effect of particle collisions on the size distribution altogether [*Lurmann et al.*, 1997]. While this assumption is reasonable when the focus of the research is on accumulation and coarse mode particles, it introduces large errors if the main interest is on the growth of the smallest particles to e.g. cloud condensation nuclei sizes. Moreover, in

large scale 3D models, the calculation of coagulation typically adds little to the computational cost of the code. The computer time required for solving coagulation can be further reduced with the help of approximative coagulation schemes, such as semi-implicit solutions [*Jacobson et al.*, 1994] or schemes approximating the coagulation equation solutions with generalized functions [*Piskunov and Golubev*, 2001].

Deposition is a particle removal mechanism which reduces the particulate mass as well as the number. Dry deposition transports aerosol particles into surfaces without precipitation and removes most efficiently particles smaller than 50 nm and larger than a few micrometers in size, the former via Brownian diffusion and the latter via inertial impaction or gravitational settling. In addition to particle size, the particle removal efficiency is dependent on the nature of the underlying surface and is more effective over rough surfaces, such as forests and urban areas, than over smooth ones, such as water and grass lands. Whereas dry deposition acts on the particles continuously, wet deposition shows distinct peaks of rapid particle removal as a result of rain, snow or cloud droplet scavenging, and following deposition to the surfaces. Nucleation scavenging inside the cloud affects only particles large enough to activate during cloud formation although smaller unactivated particles may be incorporated in cloud water if they collide with cloud droplets. Below the clouds, the removal efficiency of particles by rain drops shows a minimum at the accumulation mode size range similar to dry deposition.

A detailed quantification of the deposition mechanisms for modelling purposes is often challenging because of the complex atmospheric interactions affecting the phenomena. Although size-resolved dry deposition models exist for different kinds of surfaces [*Schack et al.*, 1985; *Gustafsson and Franzen*, 1996; *Noll et al.*, 2001; *Zhang et al.*, 2001], it is difficult to account for the effect of the underlying surface properties or the small scale atmospheric motion in detail. Moreover, the knowledge on many of the distinct mechanisms contributing to particle size distribution through wet deposition is not sufficient to allow their detailed description in numerical models. Although many models choose to simulate in-cloud and below-cloud deposition separately [*Adams and Seinfeld*, 2002; *Gong et al.*, 2003], *Guelle et al.* [1998] found out that a simple scheme not differentiating between these two and assuming a constant scavenging efficiency throughout the precipitation column reproduced the observed fluxes of ^{210}Pb particle annual deposition as well as the more detailed schemes compared. This thesis investigates aerosol dynamics at clear sky conditions and does not therefore discuss the

effect of wet deposition on particle size distribution. For particle dry deposition, the models in **Papers I-IV** consider only Brownian diffusion mechanism, whereas **Paper V** incorporates the novel semi-empirical parameterization by *Rannik et al.* [2003].

3   Numerical representation of the particle size distribution

The general dynamic equation governing the aerosol size distribution time behaviour can be written

$$
\begin{aligned}
\frac{\partial n(v,t)}{\partial t} &= -\frac{\partial}{\partial v}\left(G(v)n(v,t)\right) + \frac{1}{2}\int_0^v K(v-v',v')n(v-v',t)n(v',t)dv' \\
&\quad -n(v,t)\int_0^\infty K(v',v)n(v',t)dv' + J_0(v)\delta(v-v_0) + S(v) - R(v), \quad (1)
\end{aligned}
$$

where $n(v,t)dv$ is the number concentration of particles between volumes v and $v+dv$ at time t, $G(v)$ is the particle growth rate due to condensation/evaporation, $K(v,v')$ is the collision frequency of particles with volumes v and v', J_0 is the nucleation rate of particles with volume v_0 (since $\delta(v-v_0)$ equals unity when $v = v_0$ and is zero otherwise), and $S(v)$ and $R(v)$ describe the particle source and removal rates. Analytical solutions to the general dynamic equation exist only for a limited number of special cases, and hence aerosol dynamic models typically solve the size distribution evolution numerically. Of the great amount of numerical methods developed, the most widely used in atmospheric applications are sectional and moment approaches. One of the main objectives of this study was to investigate their accuracy and computational viability for large scale modelling purposes.

3.1   Sectional approaches

The sectional approaches approximate the continuous size distribution by a finite number of size sections and their accuracy depends essentially on the size resolution, i.e. the number of size sections that represent the particle population. In the atmosphere, the particle size distribution expands over several orders of magnitude and thus representing the whole particle distribution with a molecular resolution is not possible. For a limited particle size range of interest, such as the nucleation mode, the molecular

resolution approach offers, however, a highly accurate solution of the general dynamic equation [*Lehtinen and Kulmala*, 2003]. Despite its great computational requirements, such solution is useful in validating simpler size distribution representations [**Paper III**].

The first general formulation of the sectional method by *Gelbard and Seinfeld* [1980] assumed fixed size section locations. Later work, aiming at better accuracy with lower number of sections, has modified this assumption, and nowadays the behaviour of the size section locations upon time typically serves as a basis of the sectional approach classification. Unless otherwise noted, the discussion below assumes that the particle population within each section is monodisperse, i.e. described through a representative particle size, instead of continuous [*Gelbard and Seinfeld*, 1980].

3.1.1 Fixed sectional structure

In the fixed sectional structure, each section has a constant, characteristic size which is also the size of all the particles in that section. When the particles grow or shrink, they move to larger or smaller sections; however, the locations of the size sections stay fixed. This approach has proven an effective way to address many dynamic processes affecting the particle size distribution: If initialized correctly, the fixed structure guarantees that suitable sections exist throughout the simulation for new particles formed via nucleation or primary emissions. Furthermore, in atmospheric models that simulate particle transport, replacing the same sized particles in the adjacent spatial grid cells is straightforward with the fixed structure. These advantageous features have encouraged the wide use of the approach in applications ranging from aerosol box models [*Raes and Janssens*, 1986; *Pilinis et al.*, 1987] to 1D boundary layer models [*Fitzgerald et al.*, 1998] and 3D regional or global scale models [*von Salzen et al.*, 2000; *Gong et al.*, 2003].

Unfortunately, the conventional formulation of the fixed sectional approach does not describe the particle growth reliably [*Seigneur et al.*, 1986; **Paper III**]. The particles that grow due to condensation, evaporation or coagulation, and have at the end of the model time step reached a size that does not match exactly any of the characteristic section sizes, must be split into the existing sections. Although the most widely used splitting procedure conserves the particle total number and volume, the splitting can be viewed as placing all the mass transported to the particles in a given section into only a few of the particles. While these particles grow to a larger section, and their
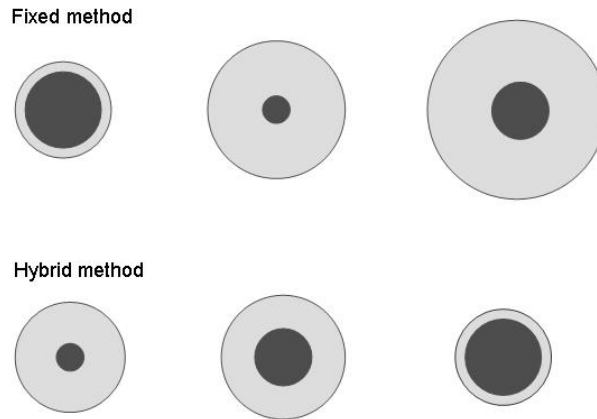
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Figure 1: Schematic figure of ordering the particle size sections in the traditional fixed sectional method and in the hybrid method. In the fixed sectional method, the total particle size, irrespective of the relative contributions of the volatile and involatile material, determines the discretization of the particles into size sections. In the hybrid method, on the other hand, the size sections are ordered and the particles discretized according to the volume of the involatile core material. Then, the total volume of the particles can in principle be distributed without a pattern from one section to another.

growth is overestimated, the others effectively remain at their old size. This feature of the fixed sectional approach, called numerical diffusion, artificially smooths the particle size distribution by widening it and lowering its peak concentrations. Numerical diffusion seldom causes problems in simulating coagulation, which typically contributes very little to particle growth, but may distort the size distribution significantly when simulating condensation. The conventional fixed structure formulation is therefore not very suitable for applications that require information on how the particle number and mass are distributed over the size domain, such as prediction of small particle growth to climatically active sizes. The many other advantageous features of the approach have, however, encouraged the development of modified structures which aim at minimizing the diffusion problem upon condensation.

One possibility to eliminate much of the artificial diffusion is to divide the particle volume to involatile core compounds, consisting of species like mineral dust, black carbon

and sulphuric acid, and to volatile condensable compounds. When the discretization of the particles into fixed size sections bases on the size of their involatile core, rather than their total size, only condensation of core compounds necessitates splitting the particles between the size sections (Fig. 1). The condensation of volatile non-core materials does not, therefore, produce numerical errors. This simple but effective improvement to the fixed sectional method, named hybrid structure by *Jacobson and Turco* [1995], is commonly used in atmospheric models [*Kärcher*, 2003; **Paper V**].

Although not used in this study, another approach to resolve the numerical diffusion problem bases on the wide range of numerical solutions developed for the advection equation. The condensation equation for a continuously distributed aerosol is

$$\frac{\partial p_i}{\partial t} = H_i p - \frac{1}{3}\frac{\partial H p_i}{\partial \mu}, \tag{2}$$

where p_i is the mass distribution of component i, H_i is its mass transfer rate, and μ is the logarithm of particle diameter. The total mass distribution and mass tranfer rate summed over all the components are denoted with p and H. The mathematical form of the latter term on the right hand side, representing the redistribution of mass, resembles the advection equation. Although many of the advection schemes fail to eliminate numerical diffusion [*Rood*, 1987], Bott's scheme [*Bott*, 1989] yields mass conserving and fairly non-diffusive solutions to the condensation equation [*Dhaniyala and Wexler*, 1996]. The scheme assumes that, instead of being constant, the mass distribution function within the sections is given by a nth order polynomial whose coefficients are interpolated with the help of the neighbouring sections. Furthermore, the scheme limits the mass fluxes by the existing mass concentrations in each section and thus prevents the arising of negative mass distribution values. The drawback of the method, employed for example in CIT air quality model [*Meng et al.*, 1998], is that it may create unrealistic peaks in the particle size distribution [*Zhang et al.*, 1999]. Another less widely used condensation solver that bases on solving the advection equation is the combined semi-Lagrangian and Lagrangian flux method PFISLM presented by *Nguyen and Dabdub* [2002].

3.1.2 Moving sectional structure

An alternative way to tackle the numerical diffusion problem is to abandon the fixed section assumption and to let the section locations move as dynamic variables in time.
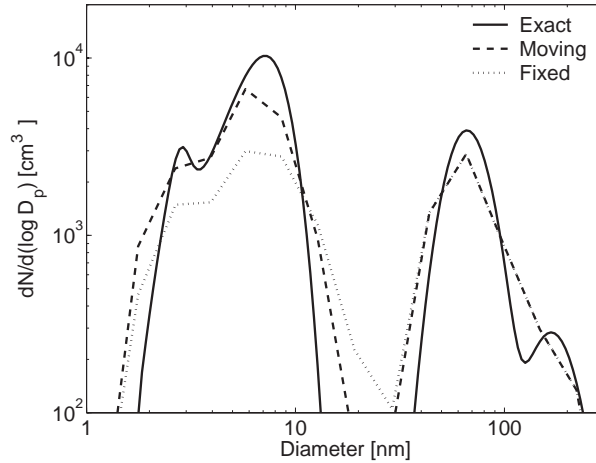
Figure 2: An example of size distribution predictions for particle formation event obtained from a fixed sectional model and a moving sectional model in which the size sections are retracked to a fixed grid after each simulation hour. The retracking method can eliminate much of the artificial lowering of nucleation mode peak compared to the fixed method but still predicts wider particle modes than the exact solution.

In the moving sectional structure, introduced by *Gelbard* [1990] and *Kim and Seinfeld* [1990], particles do not jump from one section to another as a result of condensation growth or evaporation shrinkage; instead, the characteristic size of the whole section changes. In addition to eliminating all the artificial distortion of the size distribution as far as condensation is concerned, the moving sectional structure is easy to implement and computationally efficient. These benefits have made it a widely used approach in atmospheric models [*Lurmann et al.*, 1997; *Adams and Seinfeld*, 2002; *Boylan et al.*, 2002; *Gaydos et al.*, 2003].

The main disadvantage with the moving sectional structure is its inability to treat particle formation and transport consistently. Regarding nucleation, situations can arise when the forming clusters are smaller than any of the existing section sizes. To solve the problem, aerosol dynamic models have mainly used two approaches, both tested in **Paper V**: Firstly, newly formed particles can be placed into the smallest size section and averaged with the ones pre-existing in it. The averaging, which typically conserves particle number and mass, overestimates the growth of the freshly formed particles while it somewhat shrinks the smallest pre-existing particles. If the particle formation lasts for several hours, as it typically does in the atmosphere, this approach is quite crude. The second approach, adding a new size section at the low end of

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the size distribution after a certain time interval, offers a more realistic treatment of nanocluster formation. Creating a new section at every time step produces the most reliable results but quickly increases the computational burden of the model. Although this may be acceptable in studies focusing specifically on new particle formation and growth [*Anttila et al.*, 2003], general aerosol dynamic models need to compensate for the additional burden and merge some of the sections after regular intervals [*Kumar and Ramkrishna*, 1997].

When particle transport between spatial grid cells is treated in the moving sectional structure, it is difficult to know which particles should replace which other particles. A simple solution to the problem is to treat the particle growth in the moving grid and, at the time of transport, retrack the size distribution to a fixed grid by using e.g. spline [*Lurmann et al.*, 1997] or linear interpolation [*Kumar and Ramkrishna*, 1997]. **Paper V** demonstrates, however, that if the retracking has to be done relatively often, e.g. once per simulation hour, the method eliminates only some of the numerical diffusion associated with the fixed sectional structure (Fig. 2).

3.1.3   Moving center structure

To combine the advantageous features of the fixed and moving sectional approaches, *Jacobson* [1997] introduced the moving center structure in which the section boundaries are fixed throughout the simulation but the particle sizes can vary within the sections. As in the moving sectional structure, the moving center approach eliminates numerical diffusion upon condensation and evaporation by letting the particles grow or shrink to their exact sizes. Once the particles reach the upper or lower boundary size of the section, however, they all move to the adjacent section, whose pre-existing particles they are averaged with. Fortunately, this averaging introduces very little artificial diffusion. Furthermore, sticking to fixed section boundaries assures that conveniently sized sections exist for particles formed via nucleation and primary emissions throughout the simulation, as well as enables straightforward modelling of particle transport. The moving center structure has been used in air pollution and weather forecast models [*Jacobson*, 2001]. **Paper V** applies the structure to study a new particle formation event.

Zhang et al. [1999] compared the condensation solvers used in air quality models and concluded that moving center structure reproduces the qualitative features of the size
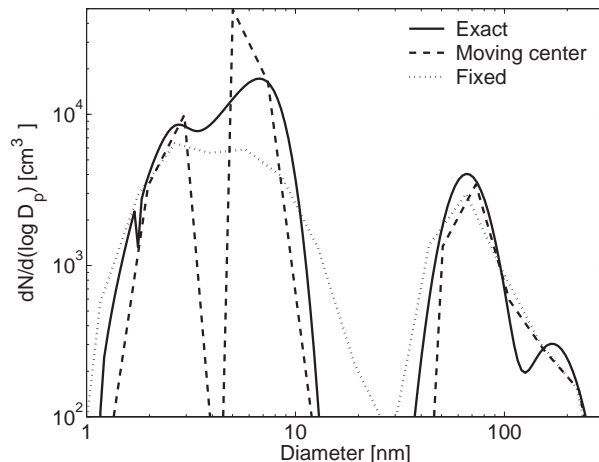
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Figure 3: An example of size distribution predictions for particle formation event obtained from a fixed sectional model and a moving center model. The moving center method eliminates practically all the numerical diffusion associated with the fixed solution but predicts an extra dent in the middle of the nucleation mode distribution.

distribution more accurately than the Bott's method or the moving sectional method that is retracked to a fixed grid after a certain number of timesteps. However, the computational requirements in air quality models necessitate the use of only few, sparsely located size sections. When the size sections are relatively close to each other, the moving center structure may produce extra dents in the size distribution [**Paper V**] as can be seen in Figure 3. The reason behind this is that the method moves all the particles which reach the upper boundary of the section to the adjacent section, and thus leaves the old one empty. Unlike typically in the case of sectional structures, increasing the number of size sections does not correct the accuracy of the results but may even favour the undesired behaviour. Moreover, the method is not suitable for detailed new particle formation studies as it suffers from built-in problems to predict the initial steps of particle growth [**Paper V**]. Averaging the moved and pre-existing particles within the smallest sections artificially delays the growth of the formed particles, and the method predicts burst-like, rather than continuous, formation of detectable particles.

3.2   Moment approaches

Rather than by the particle size distribution itself, the aerosol population can also be represented in terms of the size distribution moments. The moment method tracks the

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time dependence of the low order radial moments of the distribution defined as

$$\mu_k = \int r^k f(r) dr \tag{3}$$

where the index k refers to the kth moment and $f(r)$ is the size distribution function. The basic idea behind the method is that the derivation of a closed set of dynamical equations for the moment evolution does not require a priori assumptions of the distribution function. The conventional formulation of the moment method requires an exact closure, i.e. that the moment evolution equations involve only functions of the moments themselves. This requirement places serious restrictions on application of the method to aerosol related problems since only special cases, such as condensation in the free molecular regime, satisfy the necessary conditions for exact closure [*Frenklach and Harris*, 1987]. The problem can, however, be overcome by assuming a certain shape for the size distribution or by loosening the closure condition. As examples of the two approaches, the following sections describe the widely used modal methods and the more recent quadrature method of moments.

3.2.1 Modal methods

Motivated by particle size distribution measurements, the modal methods represent the size distribution as multiple distinct particle populations called modes. For each of the modes, the moment equation closure for relatively general atmospheric processes is achieved by assigning a mathematical form of the distribution function to the mode. In this respect, the most widely assumed mode shapes are log-normal (not used in this work) and monodisperse; the former supported by fairly good mathematical fits to observed size distribution data [e.g. *Mäkelä et al.*, 2000] and the latter by its computational convenience. Then, the characterization of each mode requires a maximum of three parameters: particle concentration, geometric mean diameter, and standard deviation, the latter of which is zero in the monodisperse case, and can be chosen constant or let to vary in time in the log-normal case. Compared to the sectional structure, the log-normal and monodisperse modal structures do not suffer from numerical diffusion and can be computationally very efficient [*Whitby and McMurry*, 1997; *Pirjola et al.*, 1999], which has led to their wide application in regional and global scale models [*Binkowski and Shankar*, 1995; *Ghan et al.*, 2001; *Wilson et al.*, 2001].

In a comparative review of size distribution algorithms, *Seigneur et al.* [1986] concluded, however, that the inherent assumption of log-normal mode shape overpredicts
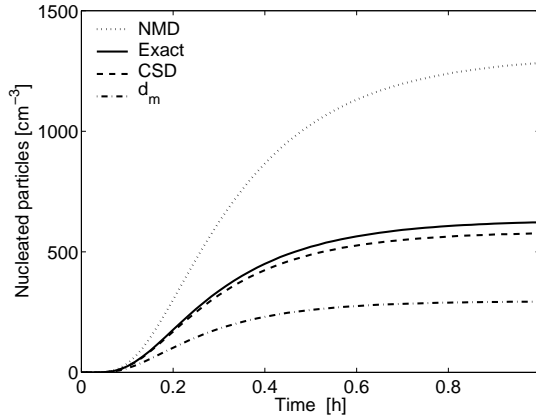
Figure 4: An example of multimodal monodisperse model predictions of newly formed particle concentrations when the locations for the pre-existing particle modes are chosen in three different ways. The most accurate results are obtained when placing the monodisperse modes at the condensation sink diameters (CSD) of the respective log-normal modes. Using the number mean diameter location underestimates the condensation and coagulation sinks, and thus predicts too strong a survival rate for the nucleated particles. Conversely, choosing the mass mean diameter as the basis of pre-existing mode locations overestimates the sinks and therefore underestimates the new particle formation.

the collision of particles. Furthermore, assuming fixed standard deviations for the modes can lead to serious errors in condensation and coagulation simulations [*Zhang et al.*, 1999]. Incapability to simulate coagulation accurately is typical also for the multimodal monodisperse structure [**Paper III**] although choosing the pre-existing mode locations wisely can greatly improve the performance of this simplified size distribution representation [**Paper IV**] as seen in Figure 4. Both the log-normal and monodisperse modal structures tend to have problems in simultaneous simulation of nanocluster formation and pre-existing particle growth. If the newly formed particles enter the smallest existing mode, instead of a new mode created for them, the log-normal approach predicts a wide unimodal distribution peaking at the location where the realistic bimodal distribution has a minimum [*Pirjola et al.*, 1999] while the monodisperse approach essentially behaves like the moving sectional structure [**Paper III**]. To correct this error, several techniques have been suggested to determine when new modes should appear at the low end of the distribution and when old larger modes should merge to control the computing burden [*Harrington and Kreidenweis*, 1998; *Whitby et al.*, 2002; *Pirjola et al.*, 2003]. In large scale models, particle transport

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with the modal structure can be problematic since the modes in each grid cell evolve independently of the neighbouring cells and it is thus difficult to know which particles should replace which other particles.

3.2.2 Quadrature method of moments

Unlike the modal method, the quadrature method of moments (QMOM) developed by *McGraw* [1997] places no assumption on the shape of the particle size distribution. Instead, it loosens the moment closure conditions, approximating the growth law integrals with n-point Gaussian quadratures, and hence extends the original method to arbitrary forms of condensation growth. Inclusion of other important atmospheric aerosol processes like coagulation, nucleation, deposition and transport [*Barrett and Webb*, 1998; *Wright et al.*, 2000] into QMOM has made the approach applicable to a wide range of atmospheric problems. Moreover, techniques to gain size distribution information from the modelled moments, such as the Randomized Minimization Search Technique (RMST) [*Heintzenberg et al.*, 1981; *Yue et al.*, 1997] that bases on minimizing the deviation of the retrieved distribution moments from the modelled moments, have further improved the usefulness of the method in aerosol simulations. With the help of the retrieved size distribution, the quadrature method of moments can predict aerosol properties relevant to their optical properties [*Yue et al.*, 1997], and cloud droplet activation [*Wright et al.*, 2002] with good accuracy. Most recently, the quadrature method of moments has been extended to internally mixed multicomponent aerosols [*McGraw and Wright*, 2003].

As with the modal method, the main advantage of the QMOM is that it requires a very low number of variables to characterize the aerosol properties: the combinations of the lowest six moments provide the particle number and mass concentrations, the characteristic radii, and the standard deviation of the distribution. This feature makes the approach computationally efficient, and hence especially suited for 3D applications [*Wright et al.*, 2000; *Yu et al.*, 2003]. The accuracy of the method in simulating aerosol dynamics is, however, strongly dependent on the extent to which the simulated processes can be expressed in terms of distribution moments. Unfortunately, comparative studies of the very recently developed QMOM against other size distribution representations are limited. Because of this and since the thesis concentrates on studying atmospheric new particle formation with a special focus on simulating the size dis-

tribution of these small particles as accurately as possible, the quadrature method of moments is not used in this work.

4 Aerosol dynamic models used in this study

The simulations for this work have been carried out with four aerosol dynamic box models. All of these models describe the major microphysical processes affecting the aerosol size distribution under clear sky conditions, i.e. nucleation, condensation, coagulation, and dry deposition.

The multimodal monodisperse model MONO32 [*Pirjola and Kulmala*, 2000; *Pirjola et al.*, 2003] has been developed to offer a physically sound but computationally effective representation of the particle dynamics in 3D Eulerian models. Its gas-phase chemistry scheme, based on the EMEP mechanism [*Simpson*, 1992], includes chemical reactions of 68 organic and inorganic compounds related to aerosol formation and growth. The model represents the aerosol distribution with four monodisperse modes, which can contain sulphate, nitrate, ammonium, organic and elemental carbon, sodium chloride, mineral dust, and water. Although the modes differ from each other in their chemical composition, all the particles within each mode have a uniform composition. In this study, MONO32 was used in **Papers I-IV** and it was further developed by modifying its description of the organic vapour condensation onto particles as well as by implementing new nucleation schemes [*Vehkamäki et al.*, 2002; *Napari et al.*, 2002], and heterogeneous nucleation on dust particles into the model.

The two fixed sectional models applied in this work were the molecular resolution model [*Lehtinen and Kulmala*, 2003], used in **Paper III**, and the Lagrangian trajectory-based air parcel model AEROFOR [*Pirjola*, 1999], used in **Papers III** and **IV**. The former describes the nucleation mode size distribution molecule by molecule, thus in this region eliminating the numerical diffusion typical to low resolution fixed grid models. Because of its great computational requirements, however, the model is mainly suitable only for detailed studies of new particle formation and growth. AEROFOR, on the other hand, is a general purpose model simulating the dynamics of atmospheric sulphuric acid – water particles. As in the case of MONO32, the gas-phase chemistry scheme in the model bases on the EMEP mechanism [*Simpson*, 1992] taking into account 67 atmospheric species. In this study, AEROFOR was further developed by updating its

nucleation schemes to those presented by *Vehkamäki et al.* [2002] and *Napari et al.* [2002].

The work done for this thesis generated a new multicomponent size-segregated aerosol dynamic model UHMA, which simulates the dynamics of particles consisting of sulphate, water-soluble and insoluble organic compounds, elemental carbon, mineral dust, ammonia, and water (**Paper V**). The model combines the most recent knowledge on new particle formation, and incorporates e.g. the Nano-Köhler theory [*Kulmala et al.*, 2003a] which describes the onset of organic vapour condensation onto newly formed nanosized clusters. The size distribution representation in UHMA can be chosen from three sectional approaches: the hybrid structure, the moving center structure and the moving sectional structure in which the sections are retracked into a fixed grid after certain time intervals. All of these approaches offer a reasonable and computationally viable way to describe particle production and transport in large scale models.

5 Review of papers

The papers included into this thesis deal with numerical modelling of the atmospheric aerosol particle size distribution. The first two papers examine dynamical processes that modify the distribution whereas the last three papers study the numerical techniques developed to solve for the size distribution dynamics. The main focus of **Papers II-IV** is on new nanosized particle formation and subsequent growth under different atmospheric conditions. **Paper I**, on the other hand, concentrates on the growth of nucleation mode particles under the influence of semivolatile organic vapours. The development and validation of a new multicomponent aerosol model, utilizing the knowledge gained from the other studies in this thesis, is reported in **Paper V**.

Paper I employs a simple multimodal monodisperse model to explore the conditions at which insoluble organic vapours are capable of growing atmospheric nucleation mode particles to cloud condensation nuclei sizes. With the help of the ratio Q/CS, where the numerator is the production rate of the condensing vapour and the denominator its condensation sink onto particles, the study searches for a realistic range of saturation concentrations for the condensable organic vapour. If the saturation concentration is very high, evaporation dominates over condensation in the smallest particle sizes resulting in no net growth. Based on model simulations and sensitivity tests, the paper

also derives an analytical expression to predict the occurence of Ostwald ripening in 10 nm particles as a function of Q/CS. This information can be used to analyze whether nucleation mode particles are able to grow to climatically active sizes or will be scavenged by coagulation.

Paper II is a study of atmospheric mineral dust aerosol, and its importance as a sink for newly formed particles and for condensable vapours. The solid mineral particles are typically not capable of absorbing the vapour molecules deposited onto their surfaces, and hence do not act as a major sink for most of the atmospheric vapours. The paper suggests, however, that heterogeneous nucleation can provide an initiating mechanism for condensation of water-soluble species onto dust. Dust particles can then influence the new particle formation both via lowering the supersaturation of the nucleating vapours and, being relatively large in size, via scavenging the nanosized clusters effectively. The paper also presents an estimate of critical condensation sink values and corresponding dust concentrations required to inhibit new particle formation altogether or to hinder the growth of nanosized clusters to 3 or 10 nm sizes.

Paper III investigates the influence of the chosen nucleation parameterization and the numerical particle size distribution representation to the results of modelling new particle formation. Because nucleation occurs in the atmosphere simultaneously with other dynamic processes, such as depletion of nucleating vapours and coagulational loss of newly formed particles, no direct conclusions on the importance of the nucleation model choice can be made based solely on the parameterizations themselves. The model results indicate, however, that the differences in nucleation rate predictions do not smooth out because of other aerosol dynamic processes but are clearly reflected in total particle concentration. Furthermore, adding ammonia to the sulphuric acid - water nucleation scheme raises the nucleation rate by several orders of magnitude, and thus makes binary nucleation an unlikely particle formation mechanism at most lower tropospheric conditions.

Paper IV introduces the concept of condensation sink diameter (CSD). This measure of the particle size distribution, which describes the loss of condensable vapours onto pre-existing particle surfaces and is proportional to the particle surface area only in the molecular regime, provides an efficient tool for analyzing the prerequisites for a nucleation event. The first application of the concept to experimental data indicates that the CSD on new particle formation days is notably lower than that on non-event days. Furthermore, defining the condensation sink diameter of the existing particle

size modes is useful in setting up model runs, especially if the model representation of the particle size distribution is simplified as is the case with multimodal monodisperse models.

Paper V describes the development of a multicomponent size-segregated aerosol dynamic model UHMA (University of Helsinki Multicomponent Aerosol model). The model incorporates recent nucleation, equilibrium, and deposition parameterizations as well as the Nano-Köhler theory [*Kulmala et al.*, 2003a] for secondary organic aerosol formation in order to simulate the formation and growth of new particles accurately. The size distribution representation in the model can be chosen from three sectional approaches, all computationally viable for large scale models, which are compared with each other in a new particle formation simulation. Moreover, a simulation of a real atmospheric nucleation event demonstrates that UHMA captures the qualitative features of the particle size distribution dynamics well. The model predicts that the composition of nucleation mode particles, originally formed by inorganic species, may be predominantly organic for particles as small as 3-4 nm in diameter.

6   Conclusions

Low volatile organic vapours are likely to be a significant contributor to the atmospheric new particle growth in forested regions. Detailed model simulations suggest that the organic volume fraction in particles of just 3-4 nm in diameter may be close to 0.5 and reach values as high as 0.8 once the particles have grown to 10 nm. The growth rate of the nanosized particles is, however, highly dependent on the ratio of the production rate of the organic vapour and its condensation sink onto the particles as well as the vapour saturation pressure above the particle surface. On the whole, model runs predict that an organic vapour responsible for 2.5-3 nm/h growth rate of nucleation mode particles should have a saturation vapour density below 10^7 cm^{-3}.

At atmospherically relevant conditions, heterogeneous ternary nucleation of sulphuric acid, ammonia, and water provides a plausible explanation for the observed coating of atmospheric dust particles with water-soluble sulphate material. Heterogeneous nucleation can, therefore, be an important prerequisite for the onset of low volatile vapour condensation onto atmospheric mineral dust, and thus control the condensation sink provided by these large particles. Through this sink for the condensable vapours and

through the coagulation sink for nanosized clusters, the dust particles can effectively prevent the growth of newly formed atmospheric particles to detectable sizes. This is especially true in desert areas where organic vapour concentrations are low. Model simulations indicate, however, that the observed dust concentrations are mostly unable to inhibit atmospheric new particle formation by homogenous ternary nucleation altogether.

When choosing an aerosol scheme for a large scale model, the main requirements are computational efficiency and accuracy in describing the particle size distribution evolution. Finding a suitable scheme which can among other processes describe the new particle formation reliably is, however, difficult. The low computational burden typically means a highly simplified size distribution representation, which often causes problems especially in the simulation of the very smallest particles. In test simulations of new particle formation events, the fixed sectional hybrid structure shows unsatisfactory performance with the size resolution typical to large scale models. Replacing the fixed section locations with moving ones and retracking the obtained size distribution to a fixed grid after certain time intervals somewhat improves the model accuracy but has the additional disadvantage of an in-built tendency to predict burst-like rather than continuous formation of detectable particles. Although suffering from the same problem with the detectable particle formation, the moving center structure eliminates almost all of the numerical diffusion associated with fixed sectional methods while inheriting its advantageous features in treating particle formation and transport. The simulations reveal, however, that this promising approach may produce undesired dents and respective peaks in the size distribution thus distorting the distribution shape within the particle modes.

On the other hand, the multimodal monodisperse model predicts the total particle concentration and the mode average sizes fairly accurately in cases when coagulation is not the dominant growth process. Although this approach is computationally very fast and easy to incorporate into large scale models, its description of the particle size distribution is very crude. When using this highly simplified particle representation, it is therefore important to carefully consider the initialization of the particle mode locations. The simulations presented in this thesis demonstrate that when the nucleation rates are sufficiently low, corresponding to e.g. rural conditions, the condensation sink diameter (CSD) provides the best estimate of the pre-existing particle diameters. In the case of high nucleation rates and, therefore, enhanced importance of particle

coagulation, the multimodal monodisperse model fails to describe the concentration of the formed new particles accurately regardless of the initial placement of the particle modes.

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