KINETICS AND DYNAMICS OF ATMOSPHERIC IONS, CLUSTERS AND AEROSOLS

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Academic dissertation

*To be presented, with the permission of the Faculty of Science
of the University of Helsinki, for public criticism in auditorium D101,
Gustaf Hällströmin katu 2, on October 13th, 2004, at 12 noon*

Helsinki 2004

Acknowledgements

The research work introduced by this thesis was carried out at the Department of Physical Sciences, University of Helsinki. I wish to thank the head of department, Prof. Juhani Keinonen for the facilities for working.

I want also to thank my supervisor Prof. Markku Kulmala for his co-operation and guidance during this work. I'm really glad that I have been able to do things in compliance with my own ideas. In the current profit striven world it is not axiomatic, even at the university.

I also appreciate the work carried out by my two other supervisors, Dos. Jyrki Mäkelä and Prof. Kari Lehtinen for their more practical guidance and help. Especially Kari has helped me much in writing the articles whereas Jyrki has offered me, among other things, his great collection of articles related to ions and charges.

Another person I wish to thank is Prof. Veli-Matti Kerminen. He is acknowledged for answering my questions, writing an excellent thesis on coagulation and also providing me with some computer codes. Dos. Liisa Pirjola is acknowledged for being my co-author and one of the creators of the AEROFOR model. I'm grateful to Dos. Hanna Vehkamäki for the course given in nucleation during the spring 2003 as well as useful answers to many of my questions. Hannele Korhonen is acknowledged for a good latex-template.

The measurement people, Dr Pasi P. Aalto and Dr Urmas Hõrrak are highly respected for carrying out the measurements without which this thesis would never have appeared. Prof. Alex Lushnikov is hailed for many interesting discussions on flux-matching and mushrooming. The following other co-authors are also acknowledged: Tuukka Petäjä, Tatu Anttila, Jussi Paatero, Markus Hanke, Frank Arnold, Hannes Tammet, Jorma Joutsensaari, Ilona Riipinen, Miikka Dal Maso and Marko Vana.

I also wish to thank Dr Aki Virkkula and Dr Jorma Jokiniemi for carefully proof-reeding my thesis and introducing many improvements, both linguistic and scientific.

Finally, I want tho thank my family, friends and especially my girlfriend Marika for helping me relax during this work. Without them my life would have been rather boring.

Kinetics and dynamics of atmospheric ions, clusters and aerosols

Lauri Kaleva Laakso
University of Helsinki, 2004

Abstract

Aerosol particle formation in the atmosphere is a significant factor affecting both the whole ecosystem and human prosperity. With the aim to understand the relevance and significance of different mechanisms contributing to particle formation, this thesis has chosen to concentrate on kinetics and dynamics of small clusters in the atmosphere. A special focus is on charged particles and ions, since they offer a way to study small particles below the size detection limit of traditional instruments. Model studies together with field and laboratory measurements offer a powerful method for investigations of particle formation mechanism. For that reason, a sectional aerosol model including charge effects was created.

The results based on ion counter, particle and particle charging state measurements as well as model studies show for the first time real, justifiable observations of the contribution of ion-induced nucleation on particle formation in the lower troposphere. The possibility of kinetic nucleation was also investigated and the results were found to support the possibility of kinetic nucleation. The most probable particle formation mechanism in the lower boreal atmosphere was found to be a combination of kinetic and ion-based nucleation. One of the key factors in ion-induced nucleation, ion production rate, was studied with two independent methods. It was found to be relatively low, 4-6 cm^{-3} s^{-1}. The effects of organic vapour and Coulomb forces on particle growth were also investigated, and both were found to be important.

Keywords: Atmospheric aerosols, ions, nucleation, particle formation and growth

Contents

List of publications

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

I Lauri Laakso, J. M. Mäkelä, L. Pirjola and M. Kulmala, "Model studies on ion-induced nucleation in the atmosphere", (2002), Journal of Geophysical Research, Vol. 107, 10.1029/2002JD002140

II Lauri Laakso, K.E.J Lehtinen and Markku Kulmala, "The effect of condensation rate enhancement factor on 3-nm particle formation in binary ion-induced and homogeneous nucleation", (2003), Journal of Geophysical Research, Vol. 108, 10.1029/2003JD003432

III Lauri Laakso, Tatu Anttila, Kari E.J. Lehtinen, Pasi P. Aalto, Markku Kulmala, Urmas Horrak, Jussi Paatero, Markus Hanke and Frank Arnold, "Kinetic nucleation and ions in boreal particle formation events", (2004), ACP-D, SRef-ID: 1680-7375/acpd/2004-4-3911 (version corrected according to referee comments).

IV Lauri Laakso, Tuukka Petäjä, Kari Lehtinen, Markku Kulmala, Jussi Paatero, Urmas Hörrak, Hannes Tammet and Jorma Joutsensaari, "Ion production rate in boreal forest based on ion, particle and radiation measurements", (2004), ACP-D, SRef-ID: 1680-7375/acpd/2004-4-3947 (version corrected according to referee comments).

V Markku Kulmala, Lauri Laakso, Kari E.J. Lehtinen, Ilona Riipinen, Miikka Dal Maso, Tatu Anttila, Urmas Hõrrak, Marko Vana and Hannes Tammet, "Initial steps of aerosol growth", (2004), ACP-D, SRef-ID: 1680-7375/acpd/2004-4-5433

1 Introduction

Aerosol particles have direct and indirect influences on the Earth's climate. The direct influence is via scattering and absorbtion of solar radiation by aerosol particles (Seinfeld and Pandis, 1998; Twomey, 1991). The indirect effect is through cloud formation and precipitation (Ramanathan et al., 2001; Cess et al., 1995; Kurten et al., 2003, e.g.). In cloud droplet formation aerosol particles act as cores for condensing water vapour. In the presence of aerosol particles the relative humidity needed for cloud droplet formation is slightly over 100% whereas without aerosol particles it is several times higher. Normally, such high relative humidities are not observed in the atmosphere so the effect of aerosol particles is indeed clearly visible. The number of available particles and their atmospheric distribution affect the properties (e.g. altitude, geographical location and droplet size) of clouds which further change the Earth's global albedo. Currently the indirect effects of aerosol particles poses one of the main uncertainties in climate change (Houghton et al., 2001).

One recent topic of the research has been the influence of solar activity on the Earth's climate (Svensmark and Friis-Christensen, 1997). Svensmark and Friis-Christensen (1997) suggested that solar wind modulates the amount of cosmic rays reaching the Earth atmosphere. The cosmic rays ionize the atmosphere by breaking up the air molecules. Because these ions may act as core ions for ion-induced (Yue and Hamill, 1979) or ion-mediated (Yu and Turco, 2000; Yu, 2002) nucleation, the concentration of ions may alter the concentration of cloud condensation nuclei and thus affect the cloud properties (Lovejoy et al., 2004).

In order to reduce the uncertainties in climatic studies, the particle formation mechanisms observed in different environments need to be investigated (Kulmala et al., 2004b). The main goal of the present thesis is to investigate neutral and charged aerosol particle concentrations and dynamics in the size region 1-3 nm. Models were utilized together with measurement results because the current instruments are not able to measure neutral particles below 3 nm.

The aims of this study are:
(1) To create a dynamical aerosol model for the investigations of charged aerosol and ion dynamics.
(2) To investigate the potential importance of ion-induced nucleation in the lower atmosphere.
(3) To understand different mechanisms contributing to charged aerosol particle and ion dynamics.
(4) To obtain ion production rate in boreal forest environment.
(5) To quantitatively and qualitatively understand the dynamics of particle formation events observed in boreal forest environment.
(6) To obtain the growth rates of aerosol particles from the measurements as a function
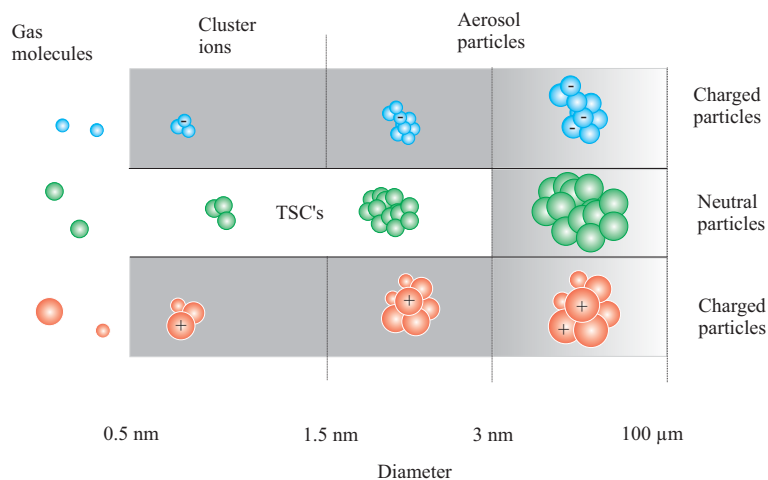
Figure 1: Cluster ions and aerosol particles. The gray area represents the size and charge range where measurements are possible. Small particles (< 20 nm) can not normally be more than singly charged. Bigger particles can carry more charges.

of particle size.

All of the measurements utilized in the current study were carried out at the SMEAR II-measurement station (61°51'N, 24°17'E, 180 m above sea level) (Vesala et al., 1998; Kulmala et al., 2001b) in Hyytiälä in southern central Finland.

1.1 Atmospheric aerosol particles and ions

In the atmosphere, there are solid or liquid obstacles called aerosol particles or ions. The distinction between aerosol particles and ions is not unambiguous. In this work, we usually refer to charged particles having diameters below 1.5 nm as cluster ions. The neutral fraction of the clusters below 3 nm are called thermodynamically stable clusters (TSC) (Kulmala et al., 2000). The term "thermodynamically stable cluster" refers to neutral clusters below the detection limit (3 nm) of the DMPS-system. Larger clusters are particles, either charged particles or neutral ones. The characterization of ions and particles is shown in Figure 1. Since cluster ions are basically different from larger charged particles they are treated separately in section 1.1.3.

1.1.1 Number concentration and size of aerosol particles

Two important properties of aerosol particles are their concentration and their size. In the atmosphere the total number concentration of aerosol particles varies by four or
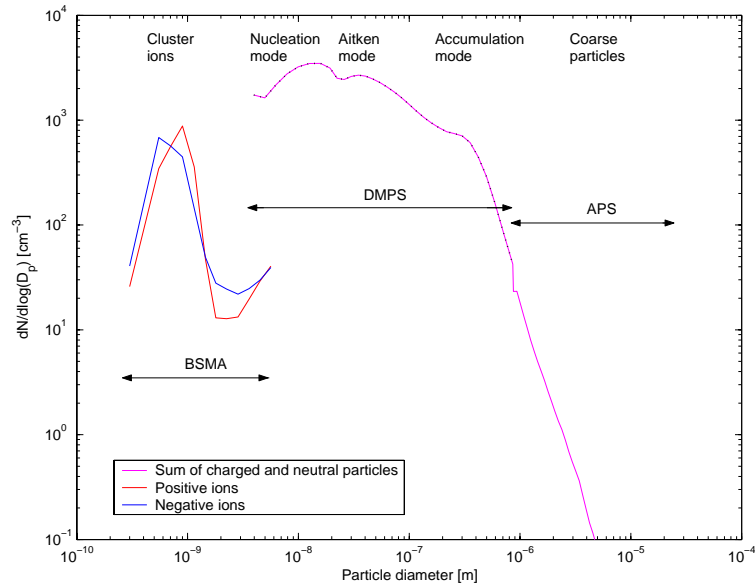
Figure 2: Aerosol and ion size distributions during the QUEST 2-campaign. The diameter ranges for different instruments corresponding to 90% relative humidity are also shown. The concentration of 3 nm particles is about 100 times higher than the concentration of 3 nm ions. This is due to the approximately 1% charging probability of the particles at this size.

five orders of magnitude. Lowest values, 1-10 cm^{-3}, have been observed in Antarctica during wintertime (Shaw, 1988; Ito, 1993) and slightly higher values, 100 cm^{-3}, during the Antarctic summer (Koponen et al., 2003). Similar numbers, 10 cm^{-3}, are also observed in the measurement station of Pallas in Northern Finland (Komppula et al., 2003). In polluted environments such as New Delhi the concentration easily exceeds 100,000 cm^{-3} (Mönkkönen et al., 2003).

Different environments are also characterized by different types of size distribution. An example of particle and ion size distributions is given in Figure 2. The distribution is an average of 25 days during the QUEST 2-campaign carried out in Central Finland in spring 2003. This figure combines measurements made with the Differential Mobility Particle Sizer (DMPS), Balanced Scanning Mobility Analyzer (BSMA) and Aerodynamical Particle Sizer (APS) (for more details on the instruments and their properties, see Section 2). Final results from DMPS and APS represent particles regardless their charge whereas BSMA measures only charged particles (or ions). Since the charged fraction of 3 nm particles is of the order of 1%, at these sizes the concentration of particles is approximately 100 times that of the ions.

Due to different physical processes, aerosol particles tend to exist in certain sizes. Small sized charged particles form so-called cluster ions which typically have diameters below 1.5 nm. Particles between approximately 1 and 30 nm form via nucleation so they are

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called nucleation mode particles. Aitken and accumulation modes result from direct emissions and growth of the nucleation mode particles whereas coarse mode particles result from direct emissions from natural and anthropogenic sources.

Generally, high accumulation mode concentrations are characteristic of polluted environments (Laakso et al., 2003) and high coarse mode concentrations of dry climates and desert areas (Chimidza and Moloi, 2000). In clean environments the size distribution is governed by nucleation and Aitken mode particles whereas in marine air the particle size distribution is bimodal and in dry, polluted environments trimodal (Jaenicke, 1993).

1.1.2 Chemical composition of aerosol particles

The chemical composition of the aerosol particles is the third important property of the particles. The atmospheric aerosol consists of a wide variety of chemical compounds (e.g. inorganic salts and acids, dust, sea-salt, organics, soot and water), mostly from natural sources but some also have anthropogenic origin (Jaenicke, 1993). The relative contribution of different sources depend strongly on time and location (Laakso et al., 2003).

The composition of aerosol particles may be extremely complicated because of the chemical complexity of the atmosphere (Mäkelä et al., 2001; Pakkanen et al., 2001; Wilson and Shuh, 1997; Luts, 1995). Much research has been carried out on this topic (see e.g. (Friedlander, 1970; Drewnick et al., 2004a,b; Kerminen, 1999; Korhonen et al., 1999; Virkkula et al., 1999)) and the contribution of some compounds (e.g. sulphuric acid, ammonia and organics) to the aerosol mass is higher than that of others. Often the composition of the particles is different in different size ranges. Smallest particle are formed via nucleation and they often consist of sulphates and organic compounds. Larger particles include in addition to sulphates and organics also soot, different metals, soil-based compounds etc. In our studies the compounds are limited to water, sulphuric acid, ammonia and organic vapours since we are interested in only the smallest size range.

1.1.3 Cluster ions

The smallest charged particles are called cluster ions. The formation of cluster ions is a very rapid process. When radiation breaks down air molecules, a positive ion and a free electron are formed. Primary ions react with molecules present in the atmosphere. The lifetime of a cluster ion, before it is scavenged by larger particles or recombination, is approximately 100 s (Hõrrak, 2001). During that time, ions undergo several continuous changes in their chemical composition. Thus, the chemical composition of a cluster ion

depends both on the concentrations of different chemical compounds present in the atmosphere and the age of the ion (Mohnen, 1977; Hõrrak et al., 1995, 1998, 2000; Eisele and Tanner, 1990; Luts and Salm, 1994; Beig and Brasseur, 2000).

Due to the different proton affinities of different chemical compounds, the compositions of negative and positive ions are different (see e.g. Amad et al. (2000) or Luts (1995)). The differences in chemical composition lead to different sizes of positive and negative cluster ions. In a boreal forest the average electrical mobilities of negative and positive ions (during the QUEST II campaign) were approximately 1.7 and 1.4 cm^2 V^{-1}s^{-1}, respectively. The corresponding masses calculated according to the method developed by Tammet (1995) were 180 and 270 amu.

Cluster ions get scavenged either by coagulation, deposition to surfaces (e.g. forest canopy), recombination or growth to larger sizes. It is also possible, that they participate on ion-induced nucleation (Paper IV). Typically the concentration of ion clusters is about 500-1000 cm^{-3}.

2 Measurements of ions and aerosol particles

In this study, several aerosol and ion instruments were utilized. Since ion counters are not familiar to most of the aerosol community, they are briefly described in this section. The measurements were mainly carried out by Dr. Urmas Hõrrak and Dr. Pasi P. Aalto. All the measurements utilized in this study were performed at the SMEAR II station.

2.1 DMPS

For sub-micron particle sizing the main instrument used was the differential mobility particle sizer (DMPS), operated 2 m above the ground and with a time resolution of 10 min. The system consists of two parallel DMPS devices: one classifying the particles between 3 and 10 nm and the other between 10 and maximum 500 nm. Both devices use a Hauke-type differential mobility analyzer (DMA) (Winklmayr et al., 1991) and a closed loop sheath flow arrangement (Jokinen and Mäkelä, 1997). The first device consists of a 10.9 cm long DMA and a TSI model 3025 CPC and the second one of a 28 cm long DMA and a TSI model 3010 CPC. Before sizing the aerosol is neutralized with a 74 MBq (2 mCi) Krypton-85 beta source.

In Figure 3 aerosol particle size distribution measured with DMPS for six days is shown. The days given here were March 24th-29th. All the days except one were particle formation days.
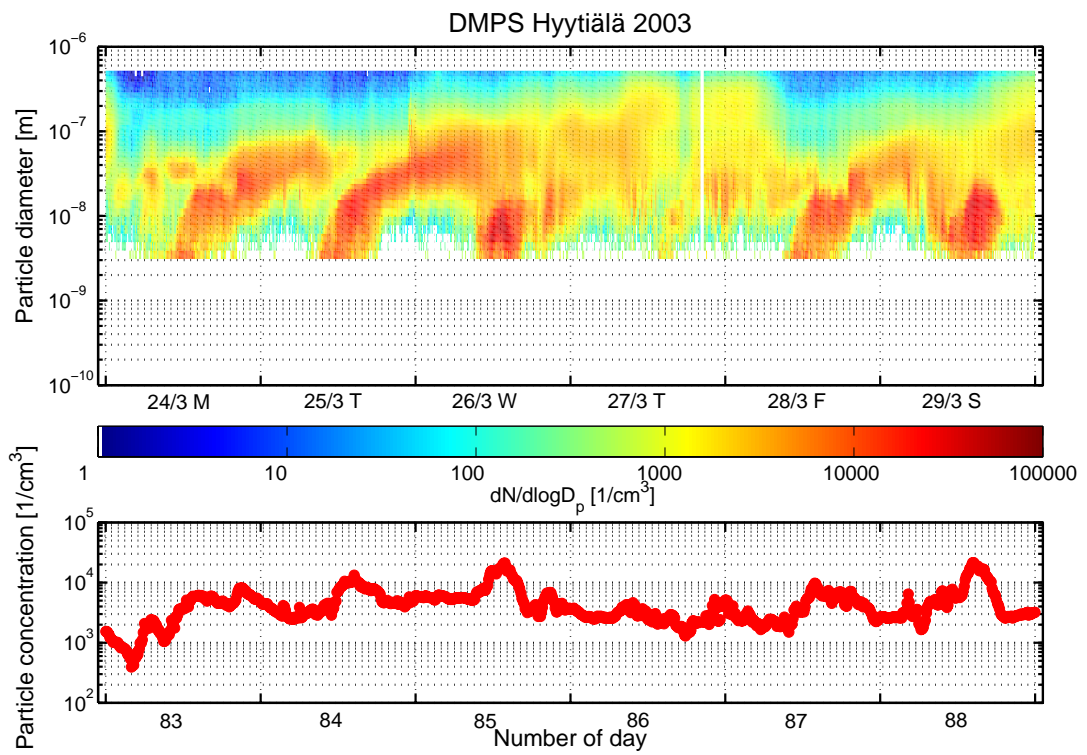
Figure 3: Particle concentration during the days 83-88 (March 24th-29th, 2003)

2.2   Charging state measurements

The natural charging state of the particles having a diameter between 3-5 nm was measured with a special DMPS setup (Mäkelä et al., 2003). There were two similar inlets, one with a neutralizer (see section 2.1), another without a neutralizer (a dummy-one). The DMPS-system switched between these two inlets every 75 seconds. When the concentration measured without the charger was divided by the corresponding charged particle concentration, the natural charging state of the aerosol was obtained. If the value is equal to one, aerosol particles are in a charge equilibrium, whereas values less than one represent undercharged particles and values larger than one indicate overcharge of the particles. The system was calibrated with 4 nm ammonium sulphate particles which were measured through both inlets. There were 33% more losses in the neutralizer compared to the dummy inlet and therefore the concentrations measured through charger were corrected by a factor of 1.5.

2.3   BSMA

The Balanced Scanning Mobility Analyzer manufactured by Airel Ltd., Estonia, consists of two plain aspiration-type differential mobility analyzers, one for positive and the other for negative ions. The two aspiration condensers are connected as a balanced bridge circuit that allows continuous variation of the driving voltage and scanning of the mobility distribution of charged clusters and nanoparticles. A large airflow rate 44 liters per second helps to suppress the loss of air ions in the inlet of the instrument. The inlet can be closed or opened for ions using a controlled electrostatic filter and the background signal is eliminated by making every second scan with a closed inlet. A mobility distribution is calculated according to the results of 9 scans performed over 3 minutes. The electric mobility range of 0.032-3.2 cm^2 V^{-1}s^{-1} is logarithmically uniformly divided into 16 fractions. The corresponding size distribution is presented by 12 fractions, logarithmically uniformly distributed in the diameter range of 0.4-6.3 nm.

BSMA measurements for the period March 24th-29th are shown in Figure 4. In this figure, cluster ions below 1.5 nm are clearly visible. Also, the size difference of negative and positive cluster ions can be observed.

2.4   AIS

The Air Ion Spectrometer (AIS, manufactured by AIREL Ltd, Estonia) measures the mobility distribution of air ions (naturally charged clusters and aerosol particles) in the range of 0.00075-2.4 cm^2 V^{-1}s^{-1}. The spectrometer consists of two identical cylindrical aspiration-type differential mobility analyzers, one for measuring positive ions and the
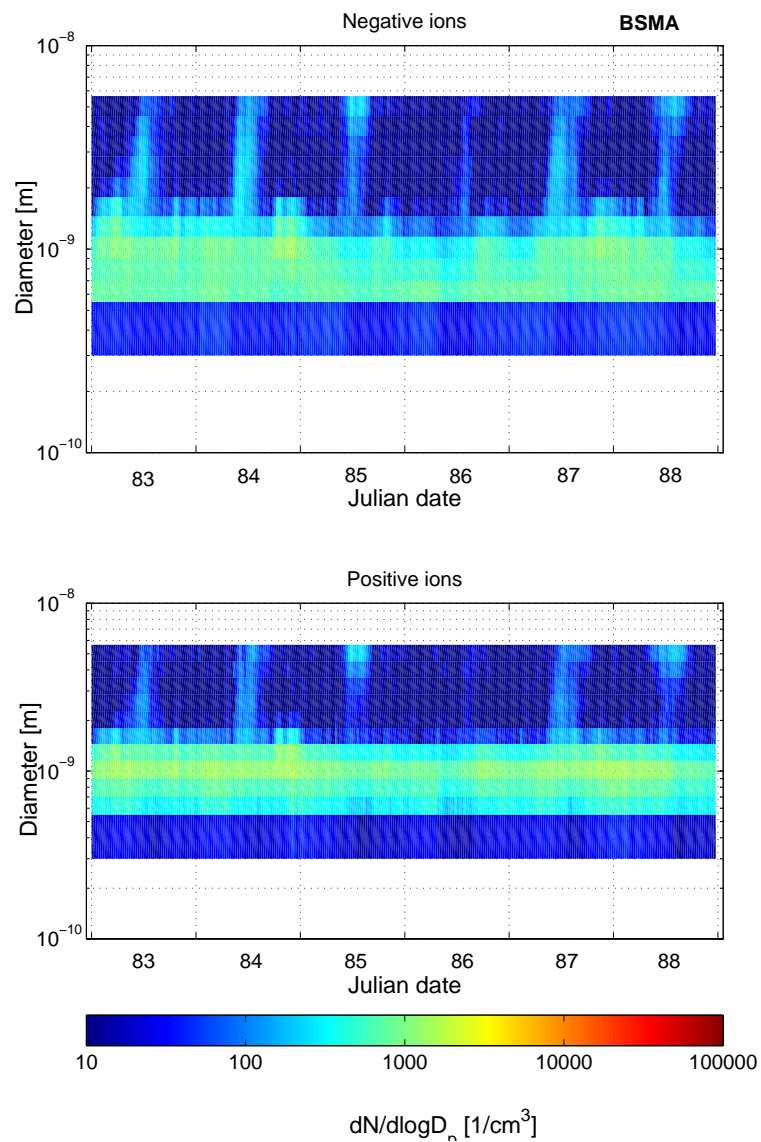
Figure 4: Ion number concentration size distributions measured by Balanced Scanning Mobility Analyzer (BSMA) during the QUEST II-campaign during March 24th-29th, 2003 (days 83-88).

second for negative ions. Each mobility analyzer has 21 collector electrodes provided with individual electrometrical amplifiers for measuring the electrical current carried by ions of different mobilities. The air sample containing ions is sucked into the mobility analyzer through the electronically controlled electrostatic filter (switched on/off). The measurements with closed inlet for ions are used for the verification of the offset level and noise of electrometrical amplifiers. Both mobility analyzers have a closed loop sheath air arrangement. The unipolar charging of aerosol particles in corona chargers and subsequent removal of charged particles by electrostatic filtration is used to create a clean sheath airflow of 1000 cm^3s^{-1}. The mobility distribution of ions is presented by 28 logarithmically uniformly distributed fractions: 12 fractions in the mobility range of 0.075-2.4 cm^2 $V^{-1}s^{-1}$ and 16 fractions (two fractions per electrometrical channel) in the range of 0.00075-0.075 cm^2 $V^{-1}s^{-1}$. The corresponding diameter range is 0.46 and 55 nm. An example of results from the AIS measurements is given in Figure 5. Similarly to the BSMA-measurements, particle formation events are clearly visible.
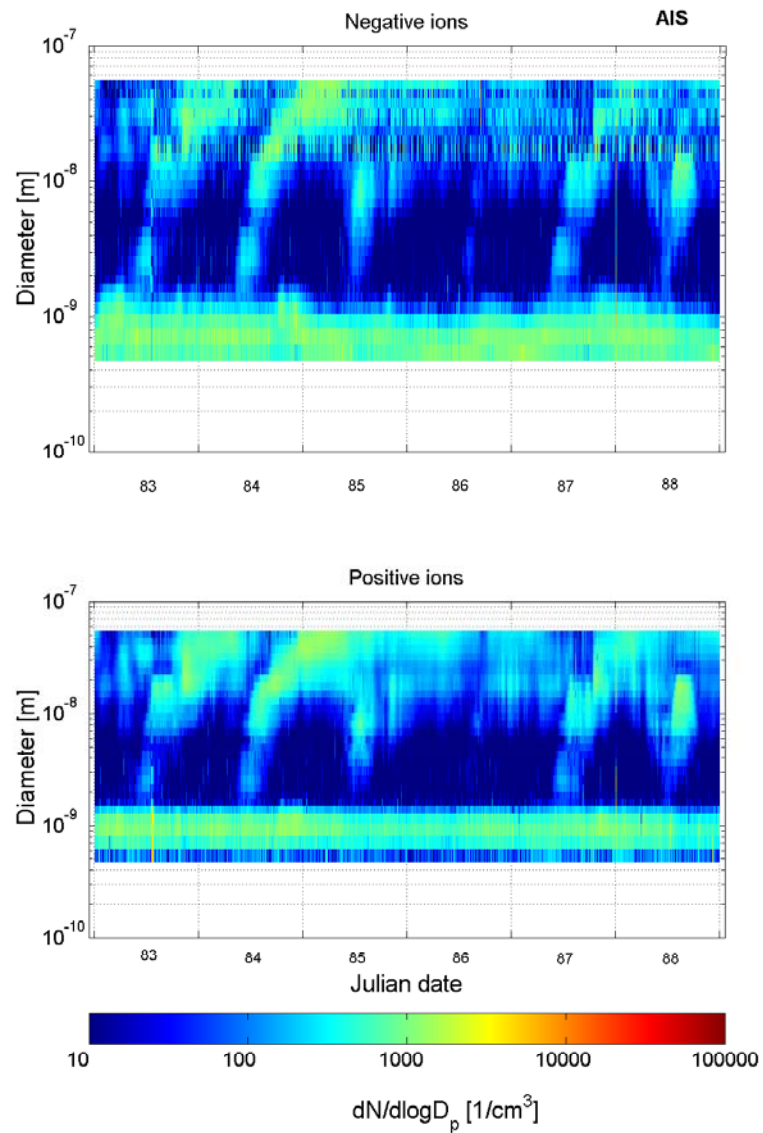
Figure 5: Ion concentration measured with an Air Ion Spectrometer (AIS) during the days 83-88 (March 24th-29th, 2003)
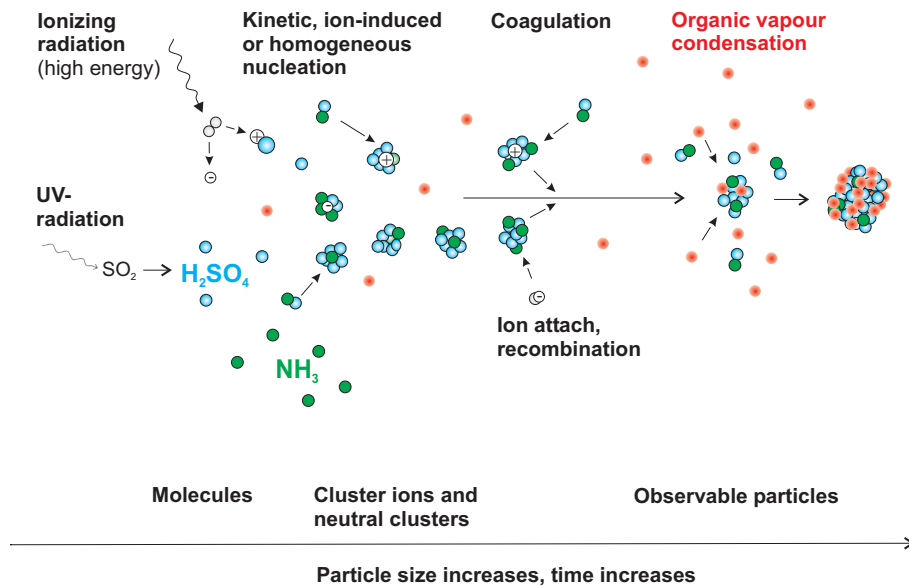
Figure 6: Aerosol and ion dynamics (Paper III)

3   Basic aerosol and ion dynamics

When aerosol and ion dynamics are modelled, several physical processes shown in Figure 6 have to be taken into account (Paper I and III). Each of these are explained in more detail below.

3.1   Ion production rate in the lower troposphere

One crucial parameter in the studies of ions and the possibility of ion-induced nucleation is the ion production rate. Ion-based particle formation is always limited by the formation rate of ions. An overview of different measurements of ion production rates in the first half of 20th century can be found in the book by Israel (1970, 1973) and Chalmers (1967). In our studies the production rate was obtained both with direct and indirect methods. The direct method is based on the measurements of radon and external radiation. The indirect method is based on the balance equation of cluster ions:

$$\frac{dn_{\pm}}{dt} = Q - \alpha n_{\pm} n_{\mp} - n_{\pm} \int_{d_p} \sum_{q=-\infty}^{\infty} \beta_{\pm}(d_p, q) N(d_p, q) dd_p \qquad (1)$$

where Q is the ion production rate, $n_{\pm}$ is the concentration of positive or negative cluster ions, α is the ion-ion recombination coefficient, $\beta_{\pm}(d_p, q)$ is the cluster ion-aerosol

particle attachment coefficient and $N(d_p, q)$ the concentration of aerosol particles of diameter d_p and charge q. Subscripts represent positive or negative ions. Ion production rate can be estimated from either of them. All of the parameters on the right hand side of the equation (1) can be measured or estimated. From the variables above $n_\pm$ is measured by an ion spectrometer, $N(d_p, q)$ with DMPS and APS and α and $\beta_\pm(d_p, q)$ being obtained from the theory. S corresponding to additional sinks caused by e.g. ion-induced nucleation, small neutral clusters or macroscopic surfaces, for instance forest canopy, can not be estimated without additional information from e.g. particle flux measurements.

The effect of hygroscopicity on particle size has also to be taken into account when estimating the cluster ion sink from number size distribution measurements. The number size distributions are usually measured with DMPS which operate at low relative humidities. Therefore the DMPS system measures dry particle diameters but in the real atmosphere RH varies between 30 and 100%, which may change the wet diameters by more than 100%. This has a significant effect on cluster ion sink caused by aerosol particles.

The indirect method based on ion and particle measurements underestimates the ion production rates especially during the day. There are several reasons for this underestimation. One reason for the under estimation is the significant number of clusters (during nucleation bursts) lying in size-range 0.5-3 nm which can not be taken into account since they are below the detection limit of DMPS. One more plausible reason for the discrepancy is the nucleation mechanism itself, if the ions are somehow involved in the nucleation process (i.e. ion-induced nucleation), there may be an additional ion sink during the nucleation days. Also, the cluster ions may be lost due to the condensational growth. In addition, the forest canopy (+ other surfaces) scavenges a portion of the cluster ions.

3.2 Nucleation

Nucleation is a starting point of the first order phase transition in which a substance changes it phase from one to another. In our case we concentrate only in the situation where the vapour phase changes to the liquid phase.

3.2.1 Homogeneous nucleation

In homogeneous nucleation one or more vapours form a cluster without a seed particle or ion (Springer, 1978). If the number of molecules exceeds a critical value (critical radius), the clusters are thermodynamically stable. The critical number of the molecules depend on conditions: concentration of the nucleating vapour(s), temperature and
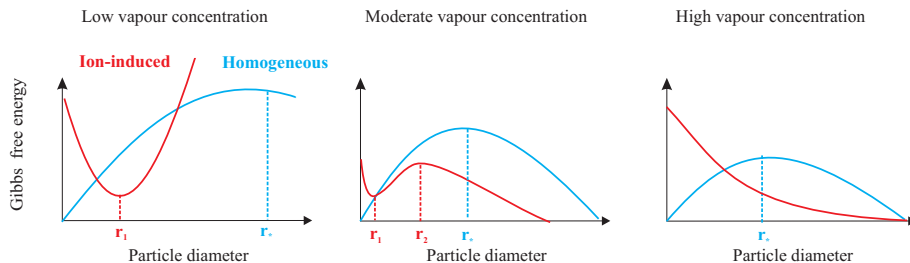
Figure 7: Gibbs free energies for homogeneous and ion-induced nucleation. Three separate figure represent different nucleating vapour concentrations. r_1 and r_2 represent the critical radii in ion-induced nucleation and r_* in homogeneous nucleation. In the case of kinetic nucleation, there is no energy barrier, so the case is similar to ion-induced nucleation with high vapour concentrations.

pressure. Mathematically, the critical radius is obtained as a unique solution of the Kelvin equation. If there are two nucleating vapours, the nucleation is called binary homogeneous nucleation.

The most frequent way to describe nucleation is based on Gibbs free energy. It describes the formation energy of a cluster based on chemical activities in vapour and liquid phase, energy committed in surface tension. Based on the capillarity approximation and the use of macroscopically measured variables it is possible to calculate critical radii and the nucleation rates for different compounds (Paper I). However, it should be kept in mind that macroscopically measured variables present a disadvantage for the use of classical nucleation theory, since concepts like surface tension and liquid density are not well-defined for clusters consisting of a couple of molecules.

Gibbs free energy curves for homogeneous and ion-induced nucleation (Section 3.2.2) are shown in Figure 7. As it can be seen that the higher the nucleating vapour concentration, the smaller is the critical radius and the lower the energetic barrier for nucleation. In our studies we used a slightly simplified version of the classical binary homogeneous nucleation theory for sulphuric acid and water, in which the critical cluster composition was parameterized (Vehkamäki et al., 2002).

3.2.2 Ion-induced nucleation

Ion-induced nucleation is a special case of heterogeneous nucleation (see section 3.2.4). In ion-induced nucleation the vapours condense around an ion. Since the energy barrier for ion-induced nucleation is lower than for the homogeneous type, nucleation should always occur via ions if they are present. However, ion-induced nucleation is always

limited by the number of ions, so if the nucleation process uses up the ions, ion-induced nucleation can not take place anymore.

In ion-induced nucleation the Coulomb force decreases the energy needed for critical cluster formation. Particles formed via ion-induced nucleation are always charged due to their origin. With low nucleating vapour concentrations there is only one solution of the Kelvin equation for the critical radius, with slightly higher concentrations two solutions and finally with very high concentrations no solutions (see Figure 7). The first two cases produce a group of stable cluster whereas in the last case all of the ions nucleate with a kinetically limited rate.

One obvious problem with the classical ion-induced nucleation theory is that it does not take into account the observed sign-preference of ion-induced nucleation (Seinfeld and Pandis, 1998; Rusanov and Kuni, 1984; Lovejoy et al., 2004). In some cases, the nucleation rate of negative ions has been observed to be up to 100 times higher than that of positive ions (Seinfeld and Pandis, 1998). The difference in nucleation rates is assumed to be a result of the effect of different dipole moments and it can not be described by classical nucleation theory (Kusaka et al., 1995).

There are also other approaches to the problem based on, for example, density functional theory (Talanquer and Oxtoby, 1995). The advantages of these methods are their ability to take into account the possible charge asymmetries caused by polarization of the molecules. Their disadvantage is their inability to give any practical results for atmospherically relevant compounds.

3.2.3   Kinetic nucleation

The third approach is based on kinetically limited nucleation where the nucleation is barrierless but limited by the vapour molecule collision rate (Paper III) (Lushnikov and Kulmala, 2001; Maksimov and Nishioka, 1999; Weber et al., 1996). The process is similar to homogeneous nucleation except that the evaporation rate of vapour molecules from the cluster is negligible compared to the collision rate. The kinetic limit is the collision rate of the molecules in certain temperature and pressure. In our studies, it is assumed that ammonium bisulphate clusters are stable, and the nucleation rate is the collision rate of these clusters. This leads to a simple system where the particle formation is only coagulation and condensation. Tedious calculations of the evaporation coefficients are not necessary due to the stability of the initial clusters. It is also possible that instead of ammonium bisulphate the clusters consist of some other stable compounds like large organic molecules.

3.2.4 Heterogeneous nucleation

Heterogeneous nucleation is a process where vapours nucleate on the surface of a pre-existing particle. Energetically heterogeneous nucleation is often, but not always more favorable than homogeneous nucleation (Fletcher, 1958). However, heterogeneous nucleation only increase the particle size and mass but not number concentration in contrast with homogeneous, ion-induced or kinetic nucleation. The difference between heterogeneous nucleation and condensation is that in case of heterogeneous nucleation there is a barrier preventing condensation. When this barrier has been exceeded, the phenomenon is called condensation.

3.3 Growth of the particles by condensation and coagulation

When a stable cluster forms, a competition between coagulation scavenging and condensational growth starts. If the particles do not grow fast enough, they are not able to reach the size of 3 nm (lower size limit of DMPS) before they are scavenged by larger particles. The vapours responsible for the condensation growth are not necessarily the same that caused the particle formation (Paper V). Sulphuric acid, ammonia and water vapours are the most likely candidates for initial particle formation (Korhonen et al., 1999; Ball et al., 1999). Recent studies, however, show the possible importance of organic vapours as well (Zhang et al., 2004).

Regardless of the chemical composition of the nucleated particles, all or a portion of them may have formed around ions resulting in charged nanometer particles. If the particles are charged, the condensation rate is enhanced due to the Coulomb interactions (Paper II) (Yu and Turco, 2000). This accelerated growth affects the competition between growth and coagulation.

Another major complication when treating nanometer-sized clusters is the lack of proper coagulation theories for small charged clusters. Currently, there are no theories for the coagulation in the presence of interparticle force fields which are valid in all size regimes. In our studies we have used simplifications based on Fuchs generalized theory (Marlow, 1980) and studies carried out by Ball and Howard (1971).

3.3.1 Condensation

Condensation is a crucial factor governing particle formation and growth. Whatever is the mechanism via which the particles are formed, they need to grow to be observed. If the growth is too slow, the clusters are scavenged by larger particles.
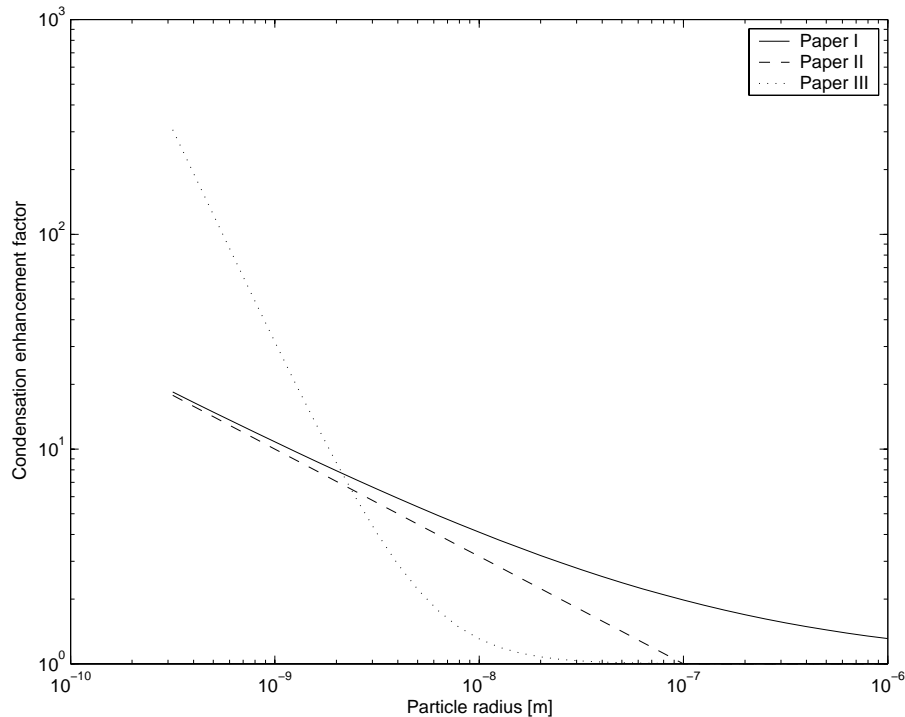
Figure 8: Condensation enhancement factors due to the Coulomb interactions used in these studies.

There are several ways to calculate condensation of vapour onto particles. One of the most frequently used is the Fuchs-Sutugin flux matching theory (Fuchs and Sutugin, 1971). It is based on the solution of the kinetic Boltzmann equation which describes the motion of molecules in the air. Since the solution of the Boltzmann equation is extremely complicated, it is often solved with certain simplifications (e.g. the mass of colliding molecules is limited to a certain range). Another simplification is used in flux-matching theories: molecules are assumed to behave according to diffusion theories far from the particle surface whereas they follow free-molecular theory close to particle surfaces. Theories matching diffusion and free-molecular fluxes at certain distances from the particle surfaces are called flux-matching theories. In case of additional force-fields (e.g. Coulomb interaction) the solutions are even more complicated. Often the effect of flux-matching theories is taken into account by introducing condensation enhancement factor which modifies the condensation coefficient for neutral particles. Only recently there have been proper theories for the calculations of the condensation enhancement due to the Coulomb or other interactions (Lushnikov and Kulmala, 2004a; Nadykto and Yu, 2003).

In Figure 8 the different approximations used for condensation enhancement in papers I-V are compared. The approximation of the Paper I is based on ion-neutral particle collisions (Hoppel and Frick, 1986). In article II the condensation enhancement factor

is based on the theory presented by Yu and Turco (2000). The main aim of this paper was to investigate the importance of condensation enhancement in the case of ion-induced and neutral nucleation. It was found that the enhancement due to Coulomb interactions was indeed of crucial importance in case of ion-induced nucleation. A recent enhancement factor developed by Lushnikov and Kulmala (2004a) has been used in Paper III for the condensation of organic vapours.

Figure 8 shows that these approximations behave differently as a function of particle size. The two first approximations underestimate the effect of the charge in the smallest size-range and overestimate the values of enhancement factor in larger sizes compared to the third one. This argument is supported by the fact that in case of charge-dipole interaction the enhancement factor is proportional to $1 + \text{const} \cdot r^{-2}$ (Lushnikov and Kulmala, 2004a). The determination of what kind of size-dependence is most correct remains a task for the experimentalists.

An additional complication to the aerosol dynamic comes from the fact that there are several gases that may condense on aerosol particles and the gases may have different chemical (e.g. vapour pressure) and electrical (e.g. polarizability) properties.

Condensation of organic vapours.
In Hyytiälä the concentrations of sulphuric acid is not high enough to explain the observed growth rates of the particles (Kulmala et al., 2001a). Thus, it is found reasonable to assume that there have to be other vapours taking part in the condensational growth, and because of their high concentration and suitable chemical properties, various organic vapours are likely candidates (Kulmala et al., 2004b; Jacobson et al., 2000). There is also recent experimental (O'Dowd et al., 2002) and theoretical (Korhonen et al., 2004) support for this assumption. The oxidation products of sesquiterpeins are one possible candidate (Bonn and Moortgat, 2003).

The use of organics lead to an additional complication due to the expected Köhler effect (Anttila et al., 2003; Kulmala et al., 2004a) since there may be a barrier preventing the condensation of organic vapours to the nanometer-sized clusters (Anttila et al., 2003; Kerminen et al., 2004). This theory has been called nano-Köhler according to the old well-known Köhler-theory applied e.g. cloud droplet formation (Köhler, 1921). Köhler theory is based on energy considerations of the particle formation. Part of the energy is bound to surface tension whereas part is related to the phase of the matter. If the clusters are small, the high curvature of the particle surface increase the saturation vapour pressure over the surface and thus hinders condensation onto the surface.

Nano-Köhler theory is based on the same effect (Seinfeld and Pandis, 1998) but in this case it is applied to nanometer sized clusters in organic vapour-ammonium bisulphate system. This theory is discussed and used in papers III and V.

In order to minimize computational burden the activation process is treated here assuming that organic vapour does not condense onto clusters having a diameter smaller

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than a certain critical diameter for condensation whereas above this size the organic vapour condenses onto clusters and larger particles irreversibly, i.e. without any thermodynamic barrier (Kerminen et al., 2004). Critical diameter is obtained from parameterization done based on detailed calculations.

3.3.2   Coagulation

Coagulation is a process where two separate particles collide and form a new, single particle. The collision rate depends on particle size, carrier gas, temperature, pressure. The material of the particles may also affect the sticking probability of the particles, i.e. the probability that two colliding particles really form a stable particle together. There are several theories that describe coagulation (Seinfeld and Pandis, 1998), in our studies we have utilized the generalized Fuchs theory which is based on flux-matching. What was said about flux-matching earlier in section 3.3.1 also applies here.

Similar to condensation, coagulation enhancement due to the Coulomb force is a critical factor. In our studies, we have used two different methods. The first is based on a simple approximation created for a free molecular regime by Howard and Ball (Howard et al., 1973; Ball and Howard, 1971) (Paper I) and the second is a brute force method where the coagulation coefficients of tiny oppositely charged clusters are assumed to reach experimentally observed ion-ion recombination rate coefficients and neutral-charged reaction rates (Paper III). Currently, there is a new flux-matching theory under construction for solving this problem (Lushnikov and Kulmala, 2004b).

3.4   Ion–aerosol attachment coefficients

The ion-aerosol attachment coefficients are calculated according to Fuchs theory (Fuchs, 1964). It is again a flux-matching theory. Other possible theories for calculating the attachment are presented, e.g., by Hoppel and Frick (1986) or Lushnikov and Kulmala (2004a). The calculations of ion-aerosol particle attachment coefficients are of great importance because they are one of the key parameters governing the possibility to detect ion-induced nucleation in the atmosphere. We have used measured cluster ion properties as input values for the calculations of attachment coefficients.

4 Aerosol and ion dynamics model

4.1 General dynamic equation

Several methods to represent the aerosol particle population in the models (or observations) can be used (see e.g. Seinfeld and Pandis (1998); Korhonen et al. (2003); Jacobson (1995)). In modal models the particles are represented by a distribution of set functional (most often lognormal) form. The benefit of the modal models is the low number of differential equations needed to explain wide size ranges which is necessary for many applications needing high computational efficiency. Another approach uses the sectional models which are intuitive and easy. In sectional models particle sizes are split into certain interacting size intervals. The problem with sectional models is that they suffer from numerical diffusion (Korhonen et al., 2003). Numerical diffusion is a phenomenon where distributions get wider due to the discretisation of a continuous system. A sectional model with a solid grid is utilized throughout this thesis.

Combining in a sectional model the different phenomena described in Section 3 one obtains a set of differential equations (Paper I) that is called the general dynamic equation (GDE) (Pirjola, 1999; Raes and Janssens, 1986; Friedlander, 1977):

$$
\begin{aligned}
\frac{dN_{\mathrm{i}}^{\mathrm{q}}}{dt} &= I^{\mathrm{q}} \frac{n^* - n_{\mathrm{i-1}}}{n_{\mathrm{i}} - n_{\mathrm{i-1}}} \delta_{n^*,]n_{\mathrm{i-1}}, n_{\mathrm{i}}]} + I^{\mathrm{q}} \frac{n_{\mathrm{i+1}} - n^*}{n_{\mathrm{i+1}} - n_{\mathrm{i}}} \delta_{n^*,]n_{\mathrm{i}}, n_{\mathrm{i+1}}]} \\
&+ \frac{AC_{\mathrm{i-1}}}{n_{\mathrm{i}} - n_{\mathrm{i-1}}} N_{\mathrm{i-1}}^{\mathrm{q}}(t) c_{\mathrm{b}}(t) - \frac{AC_{\mathrm{i}}}{n_{\mathrm{i+1}} - n_{\mathrm{i}}} N_{\mathrm{i}}^{\mathrm{q}}(t) c_{\mathrm{b}}(t) \\
&+ \sum_{l,m=qmin}^{qmax} \sum_{j=1}^{i} \sum_{k=j}^{i} \frac{K_{j,k}^{l,m}}{1 + \delta_{j,k}\delta_{l,m}} N_{j}^{l}(t) N_{k}^{m}(t) \frac{((n_j + n_k) - n_{\mathrm{i-1}})}{(n_{\mathrm{i}} - n_{\mathrm{i-1}})} \delta_{n_j+n_k,]n_{\mathrm{i-1}}, n_{\mathrm{i}}]} \delta_{l+m,q} \\
&+ \sum_{l,m=qmin}^{qmax} \sum_{j=1}^{i} \sum_{k=j}^{i} \frac{K_{j,k}^{l,m}}{1 + \delta_{j,k}\delta_{l,m}} N_{j}^{l}(t) N_{k}^{m}(t) \frac{((n_{\mathrm{i+1}} - (n_j + n_k))}{(n_{\mathrm{i+1}} - n_{\mathrm{i}})} \delta_{n_j+n_k,]n_{\mathrm{i}}, n_{\mathrm{i+1}}]} \delta_{l+m,q} \\
&- N_{i}^{q}(t) \sum_{p=qmin}^{qmax} \sum_{j=1}^{nclass} K_{i,j}^{q,p} N_{j}^{p}(t) \\
&+ \eta_{\mathrm{i},+}^{\mathrm{q-1}} n^+ N_{\mathrm{i}}^{\mathrm{q-1}}(t) + \eta_{\mathrm{i},-}^{\mathrm{q+1}} n^- N_{\mathrm{i}}^{\mathrm{q+1}}(t) \\
&- \eta_{\mathrm{i},-}^{\mathrm{q}} n^- N_{\mathrm{i}}^{\mathrm{q}}(t) - \eta_{\mathrm{i},+}^{\mathrm{q}} n^+ N_{\mathrm{i}}^{\mathrm{q}}(t)
\end{aligned}
\tag{2}
$$

where the subscripts refer to sizes and the superscripts to charges. $N_{\mathrm{i}}^{\mathrm{q}}$ is the number concentration in size class i and charge class q. I^{q} is the particle formation rate, C_{i} the condensation rate and $K_{\mathrm{j,k}}^{\mathrm{l,m}}$ is the coagulation coefficient between particles of size j and k with charges l and m and A is the enhancement factor in condensation due to the image forces on charged particle. $\eta_{\mathrm{i},\pm}^{\mathrm{q}}$ is the attachment coefficient between ions and aerosol particles and n^+ and n^- are the number concentrations of positive and

negative ions. *nclass* is the number of size classes and *qmin* and *qmax* are the lower and upper limits of charge classes in corresponding particle sizes.

The first line presents particles formed by kinetic, homogeneous or ion-induced nucleation, second line particles coming to size class i from size class $i-1$ via condensation, the third and fourth line give sources via coagulation and the fifth line the loss of particles caused by coagulation. The sixth and the seventh line are the source and sink terms due to the ion-aerosol attachment. The reason for having two terms in each case except coagulation loss is that the particles moving between size classes are divided between the two closest size classes (Pirjola et al., 1999). Because of this, the size class i gets particles from the size interval $[i-1, i]$ and $[i, i+1]$. Symbols of type n_j refer to number of sulphuric acid molecules in certain size class.

The concentration of the particles having a certain size and charge increase due to the condensation from the smaller sizes and decrease due to the condensation to larger sizes. Particles can also appear or get lost due to coagulation. Their charge can also change due to the charging or discharging events. The smallest particles appear due to nucleation.

4.2 The modelling of field measurements

The most powerful method to study atmospheric aerosols is a combination of models, theoretical work, experiments and field measurements.

In our investigations the ion and particle measurements are simulated with a model (Papers I and III). Most of the input parameters are taken from the measurements. These include the background aerosol particle distribution of particles above 40 nm, relative humidity, temperature, sulphuric acid concentration and ion production rate. All the measurements used in this study were carried out at the SMEAR II-measurement station. These experimental results are utilized together with the models.

One of the most interesting study was the combination of model calculations and experiments carried out during the QUEST 2-campaign at Hyytiälä (Papers III-V). In this study, it was found that in the case of clean air masses, particles were sometimes overcharged which indicates that ions may have taken part in the particle formation process. The quantitative investigations of the importance of different contributions remains a future task.

5 Review of the papers

The thesis consist of five articles published in peer-reviewed journals.

- **Paper I**

  In this paper a new model for ion-induced nucleation and charged aerosol dynamics is presented. The results indicate that ion-induced nucleation is able to produce new particles if the pre-existing particle concentration is sufficiently low. Also, when only positive or negative ions nucleate a large amount of particles in observable sizes was produced. In this article, the possibility of neutral clusters below the detection limit of the DMPS was discussed, corresponding to the recent idea of thermodynamically stable clusters. In some simulated conditions, fair agreement with observed particle formation events in boreal forest environment was achieved. According to the results, in certain situations ion-induced nucleation changes the charge distribution of the particles, which may allow the observation of ion-induced nucleation in the atmospheric conditions. Based on the results from this article, such measurements were carried out during the QUEST 2-campaign.

- **Paper II**

  The effect of charges on condensation of polar molecules onto particles was investigated. The main aim was to find out the upper limit of the effect and its significance on nucleation mode particle growth dynamics. It was found that the enhancement factor plays an important role in particle formation in the case of ion-induced nucleation whereas in case of neutral nucleation the effect was found to be insignificant.

- **Paper III**

  In this paper particle formation mechanisms in boreal forests were investigated based on measurements and model calculations. Kinetic nucleation together with nano-Köhler theory was found to be able to explain the particle formation and charge characteristics of the particles and ions. However, an excess of negative 1.5-3 nm ions compared to positive ions and the observed overcharge in 3-5 nm particles indicated the importance of ions in the process. The relative importance of ion-based particle formation was found to be probably much lower than the importance of kinetic nucleation. Because of a lack of microphysical knowledge, different mechanisms which may produce the difference between negative and positive ions were reckoned. One possible candidate was found to be different growth rates of negative and positive particles. The results of this article were also found to support the existence of thermodynamically stable clusters.

- **Paper IV**

  In the fourth paper the ion production rates in a boreal forest were studied based on two different methods: 1) cluster ion and particle concentration measurements, 2) external radiation and radon concentration measurements. Both methods were able to produce reasonable estimates for ion production rates. The average ion production rate calculated from aerosol particle size distribution and

air ion mobility distribution measurements was 2.6 cm^{-3} s^{-1} and based on external radiation and radon measurements 4.5 cm^{-3} s^{-1}. The contribution of radon was about 0.5 cm^{-3}s^{-1}, the rest was produced by cosmic rays. The results from this article were utilized in Paper III.

- **Paper V**
  The fifth article focused on the initial steps of aerosol particle growth. It was found that the first results support the nano-Köhler activation mechanism. The growth rates of the atmospheric particles were obtained from ion counter and DMPS measurements. A clear size dependence of the growth rates was achieved. However, the obtained growth rates were also possibly affected by the diurnal cycle of the unknown condensing vapour.

6 Conclusions

Ion concentration and charge distribution of the aerosol particles offer an effective method to study particle formation mechanisms. With conventional instrumentation the lowest measurement limit of neutral particles is 3 nm whereas in the case of ions the clusters can be measured down to the molecular size. Based on ion measurements and model calculations particle formation and growth in diameter range 1.5-3 nm was studied. The major results of this thesis were the following:

(1) A model was developed for the simulation of the atmospheric particles formation events. The model was able to reproduce observed number concentrations and charge distributions during the particle formation events.

(2) Ion-induced nucleation is able to produce aerosol particles in boreal boundary layer.

(3) The enhanced condensation rates due to Coulomb forces have a significant importance, but only in the case of ion-induced nucleation.

(4) As ion-induced nucleation relies on the ion production rate, this necessary piece of information was obtained from the measurements. The ion production rate was found to be approximately 4-6 cm^{-3} s^{-1} of which only about 10% was due to the radon decay.

(5) Kinetic nucleation was able to explain the observed particle formation events in the boreal forest. However, also ion-induced nucleation was found to contribute to the process. The relative magnitudes of the two mechanisms remain unclear. It seems that neutral nucleation is more dominant than the ion-induced mechanism.

(6) Measurements supported the idea of nano-Köhler theory, at least to a certain degree. It was also found that the concentration of sulphuric acid was too low to allow the particles grow to observable sizes.

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