ON THE GROWTH OF ATMOSPHERIC NANOPARTICLES BY ORGANIC VAPORS

TAINA YLI-JUUTI

Division of Atmospheric Sciences
Department of Physics
Faculty of Science
University of Helsinki
Helsinki, Finland

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Abstract

Atmospheric aerosol particles affect the visibility, damage human health and influence the Earth’s climate by scattering and absorbing radiation and acting as cloud condensation nuclei (CCN). Considerable uncertainties are associated with the estimates of aerosol climatic effects and the extent of these effects depends on the particles size, composition, concentration and location in the atmosphere. Improved knowledge on the processes affecting these properties is of great importance in predicting future climate.

Significant fraction of the atmospheric aerosol particles are formed in the atmosphere from trace gases through a phase change, i.e. nucleation. The freshly nucleated secondary aerosol particles are about a nanometer in diameter, and they need to grow tens of nanometers by condensation of vapors before they affect the climate. During the growth, the nanoparticles are subject to coagulational losses, and their survival to CCN sizes is greatly dependent on their growth rate. Therefore, capturing the nanoparticle growth correctly is crucial for representing aerosol effects in climate models. A large fraction of nanoparticle growth in many environments is expected to be due to organic compounds. However a full identification of the compounds and processes involved in the growth is lacking to date.

In this thesis the variability in atmospheric nanoparticle growth rates with particle size and ambient conditions was studied based on observations at two locations, a boreal forest and a Central European rural site. The importance of various organic vapor uptake mechanisms and particle phase processes was evaluated, and two nanoparticle growth models were developed to study the effect of acid-base chemistry in the uptake of organic compounds by nanoparticles. Further, the effect of inorganic solutes on the partitioning of organic aerosol constituents between gas and particle phase was studied based on laboratory experiments.

Observations of the atmospheric nanoparticle growth rates supported the hypothesis of organic compounds controlling the particle growth. The growth rates of particles with diameter < 20 nm vary with particle size, and the processes covering the uptake of organic vapors and limiting the nanoparticle growth were concluded to be size dependent. Formation of organic salts in the particle phase is likely to play a role in nanoparticle growth, however, according to the model predictions, it does not explain the uptake of semi-volatile organic compounds entirely. Small amount of inorganic salt does not seem to affect the volatility of organic acids, however with an increased inorganic content the case is not as clear.

Keywords: condensational growth, new particle formation, organic aerosol, nanoparticles
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This thesis consists of an introductory review, followed by 5 research articles. In the introductory part, these papers are cited according to their roman numerals.


1 Introduction

The atmosphere surrounding the Earth consists of a mixture of gases and small solid and liquid particles. Earth’s atmosphere is, thus, an example of an aerosol. By definition, aerosol is a mixture of solid or liquid particles suspended in a gas. Atmospheric aerosol particles vary in size from about a nanometer to hundreds of micrometers, and their number concentrations in planetary boundary layer vary typically from $10 \text{ cm}^{-3}$ in clean environments to $10^{6} \text{ cm}^{-3}$ in polluted areas (Seinfeld and Pandis, 2006).

Life on Earth is affected by atmospheric aerosol particles in many ways. Aerosol particles can be carried in the respiratory system with inhalation of air, and can, therefore, cause adverse health effects (Dockery and Pope, 1994; Nel, 2005). They scatter light and in high concentrations deteriorate visibility. Atmospheric aerosol particles also affect the climate by influencing the Earth’s radiation balance through scattering and absorbing radiation (Lesins et al., 2002). Further, aerosol particles are needed as nuclei for cloud droplet formation in the atmosphere. Through this role as cloud condensation nuclei (CCN), aerosol particles have indirect effects on climate as they influence the properties and lifetimes of clouds (Lohmann and Feichter, 2005). While greenhouse gases have a warming effect, aerosol particles are estimated to, on average, cool the climate. Intergovernmental Panel on Climate Change (Solomon et al., 2007) has estimated that the cooling effect caused by aerosol particles since the preindustrial times may have counteracted one third of the warming effect of the greenhouse gases. However, of all the climate forcers, most uncertainty in climate change is related to the effects of aerosol particles (Solomon et al., 2007). Quantifying the aerosol climatic effects is challenging as the effects depend on the particle size, composition, concentration and location in the atmosphere – all of which can vary widely depending on the sources of the particles, transportation of the particles and evolution of the particle population in the atmosphere.

Atmospheric aerosol particles originate from both anthropogenic and biogenic sources. They are emitted into the atmosphere, for example, from combustion processes, biomass burning and as suspensions of dust from the ground. Aerosol particles can also be formed in the atmosphere from ambient trace gases through a phase change. These particles are called secondary aerosol particles, opposite to the primary particles emitted into the atmosphere in the particulate form. Chemical composition of particles depends on their sources and processing in the atmosphere. Fine particles (diameter
< 1 µm), which are of most interest related to climate, contain various inorganic and organic constituents. In many environments organic compounds account for a major fraction of fine particle mass (Jimenez et al., 2009).

The organic particulate material can either be in the primary particles when they are emitted into the atmosphere or result from the transport of gas phase compounds to the particle phase. Secondary organic aerosol (SOA) is formed when volatile organic compounds (VOC), which are emitted into the atmosphere as gases, are transformed into less volatile species in the atmosphere through chemical ageing, with the resulting compounds condensing on the particles. SOA is estimated to account for the majority, 70 %, of global particulate organic carbon mass, although considerable uncertainties are related to the atmospheric organic aerosol budgets (Hallquist et al., 2009). Furthermore, most of the SOA mass is of biogenic origin, following from VOCs emitted e.g. from vegetation, although also likely influenced by the anthropogenic factors (Hallquist et al., 2009; Hoyle et al., 2011). Atmospheric VOCs include a large variety of hydrocarbons, of which the most significant group for SOA formation is monoterpenes (C_{10}H_{16}) (Kanakidou et al., 2005; Hallquist et al., 2009), although it has been suggested that most organic compounds may produce SOA upon oxidation (Kroll et al., 2011).

Regional secondary aerosol particle formation takes place frequently in the atmosphere in various environments (Kulmala et al., 2004c). In these new particle formation events the particles are formed by nucleation from gas phase precursors, followed by condensational growth towards larger sizes. These nanoparticles are estimated to make up a significant fraction of aerosol particle number concentration on a regional scale (Merikanto et al., 2009). The freshly formed nanometer-sized particles are too small to affect climate and they need to grow tens of nanometers in order to act as CCN (Dusek et al., 2006). During the growth, the nanoparticles are subject to coagulational losses to larger particles, and the fraction of the nanoparticles that survives to CCN sizes depends on how fast they grow relative to the rate of coagulational losses (Kerminen and Kulmala, 2002; Kuang et al., 2009). Due to the strong size dependence of coagulation rate, the growth rate of particles smaller than 20 nm by diameter is particularly important. Therefore, correct representation of nanoparticle growth is crucial for depicting the aerosol effects in climate models (Riipinen et al., 2011).

In many environments a large fraction of the growth of the freshly nucleated particles is due to condensation of organic vapors on the particles (Kulmala et al., 2004c; Hallquist et al., 2009). Therefore, the formation of SOA is of great importance for the growth of
secondary aerosol particles. Unfortunately, identification of organic compounds that contribute to the nanoparticle growth, information on the thermodynamic properties of these compounds and knowledge on particle and gas phase chemical and physical processes affecting the uptake of organic compounds by nanoparticles are incomplete to date. This is affected by the enormous number of different organic compounds in the atmosphere and the challenges in measuring the chemical composition of nanoparticles and thermodynamic properties of the related organic compounds (Kanakidou et al., 2005; Goldstein and Galbally, 2007; Kulmala and Kerminen, 2008; Hallquist et al., 2009). Some atmospheric observations suggest that the particle size is more important than the chemical composition for CCN activation (Dusek et al., 2006), and simplified growth rate parameterizations (e.g. Häkkinen et al., 2013) may be sufficient for capturing the contribution of secondary aerosol particles to CCN concentrations in the climate models. However, the growth rate of a particle is affected by the thermodynamic properties of the condensing compounds and by the mechanisms involved in this uptake. Therefore, developing such parameterizations requires observations of the variability of particle growth rates with ambient conditions and understanding of the chemical and physical processes limiting the particle growth.

This thesis focuses on the growth of atmospheric secondary aerosol particles formed during regional new particle formation events and the thermodynamic processes and properties related to the particle growth by organic compounds. The aims of this thesis are

1) to explore the variation in the growth rates of atmospheric nanoparticles at different ambient conditions and as a function of particle size,

2) to investigate the possible effects of particle phase chemical processes on nanoparticle growth by organic compounds,

3) to develop a nanoparticle growth model where particle phase acid-base chemistry is taken into account and use it for studying the effect of salt formation on condensation of organic acids and bases, and

4) to study the effect of inorganic constituents on the volatility of organic aerosol and test the performance of current state-of-the-art thermodynamic model for such mixed system.

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The variability of atmospheric nanoparticle growth rates is studied based on observations at two locations: a boreal forest site and a rural Central European site (Paper I, Paper II). The effect of particle phase processes on particle growth is addressed by the review of recent observations and by means of numerical modeling (Paper III, Paper IV). The effect of particle composition on the volatility of organic aerosol is examined based on laboratory experiments of atmospherically relevant mixed particles containing an organic acid and ammonium sulfate (Paper V).
2 Atmospheric new particle formation

New particle formation (NPF) refers to the formation of nanometer-sized particles through phase change from gas to particles. In atmospheric boundary layer, regional NPF events, i.e. bursts of nucleated nanoparticles and their subsequent growth, are observed frequently in various environments ranging from remote boreal forest to urban and from coastal to high-altitude sites (Kulmala et al., 2004c). During a typical NPF event, a new mode of nanometer sized particles (nucleation mode) appears during daytime and the growth of the particles can continue over the night (Fig. 1). The observations of NPF events in the atmosphere are most often based on stationary measurements, and, therefore, the extension of NPF events over several hours suggests that NPF typically happens on a spatial scale of tens or even hundreds of kilometers (Kulmala et al., 2004c).

Once formed, the nanoparticles are part of the aerosol particle population subject to various dynamic processes (e.g. Seinfeld and Pandis, 2006). Most importantly, the particles can grow or decrease in size through condensation and evaporation of vapors to/from the particle, and collide and coagulate with other particles. The removal of particles from the atmosphere takes place by dry or wet deposition onto the surfaces. The coagulation rate is strongly size-dependent, and the smaller the nucleation mode particles, the faster they are scavenged by collisions with larger pre-existing particles. In order for NPF event to be observed, the nucleated particles need to grow fast enough compared to the rate of their coagulational losses (Weber et al., 1997; Kerminen et al.,

![Figure 1: Aerosol particle size distribution measured with DMPS (see Sect. 2.1) on April 3rd 2004 in Hyytiälä. The color indicates the particle number concentration (N) in format dN/dlog(dp), where dp is the particle diameter.](image)
2001; Kerminen and Kulmala, 2002; Kuang et al., 2010). The pre-existing particles also form a condensational sink (CS) for the nucleating and condensing vapors, and a high pre-existing particle concentration can prevent NPF from occurring.

Molecular clusters can form when trace gas molecules collide with each other. If the clusters break back to monomers more likely than gain more molecules, new particles are not formed in substantial numbers. In the atmosphere, both charged and neutral clusters of diameters less than two nanometers are observed also outside NPF events (Paper I; Kulmala et al., 2007; Hirsikko et al., 2011; Kulmala et al., 2013) as predicted theoretically (Kulmala et al., 2000). Formation of secondary particles by nucleation refers to the formation of such molecular clusters from atmospheric trace gases that are more likely to grow than evaporate back to gas phase (e.g. Seinfeld and Pandis, 2006). Formation of a small cluster involves large surface energy, and, therefore, saturation ratios (ratio of the partial pressure to saturation vapor pressure) that exceed unity are needed. Atmospheric trace gas concentrations are low, and thus only compounds with very low volatility can produce new particles in the atmosphere. The exact mechanisms of atmospheric nucleation are not known yet, however strong evidence exists on sulfuric acid being the driving compound, likely with the assistance from basic compounds such as ammonia and amine (Weber et al., 1995; Kulmala et al., 2006; Kuang et al., 2008; Kurten et al., 2008; Ortega et al., 2008; Sipilä et al., 2010; Kulmala et al., 2013). Organic vapors are present in the atmosphere more abundantly than sulfuric acid, and speculation of nucleation involving oxidized organic compounds have been presented (Metzger et al., 2010). However, due to their higher saturation vapor pressures compared to sulfuric acid, organic compounds seem to be less likely candidates (Zhang and Wexler, 2002).

2.1 Instruments used for studying atmospheric new particle formation

The freshly formed secondary aerosol particles are of the order of nanometers in diameter, and the instruments used for studying them are required to detect particles down to these very small sizes. In this thesis, particle size distributions measured with three different types of instruments were used: Differential Mobility Particle Sizer (DMPS) (Paper I; Paper II), Air Ion Spectrometer (AIS) (Paper I; Paper II) and Balanced Scanning Mobility Analyzer (BSMA) (Paper II).
The DMPS measures the total particle size distribution, including both neutral and naturally charged particles (Aalto et al., 2001). In the DMPS, the particles are first passed through a dryer and a neutralizer, then led to a differential mobility analyzer for size classification based on their electrical mobility and, finally, to a condensation particle counter (CPC) where their number concentration is measured. The detection limits of DMPS vary between setups: in Paper I particles with mobility diameter (Mäkelä et al., 1996) of 10-1000 nm were detected, while in Paper II the lower detection limit was 3 nm.

The AIS (Mirme et al., 2007) and the BSMA (Tammet, 2006) also use mobility analyzers for the particle size classification, but the particle concentration is measured based on the electrical current carried by the particles to the collectors on the walls of the mobility analyzers. Since the AIS and the BSMA do not employ a neutralizer for charging the particle sample, these instruments measure only the naturally charged particles, i.e. negatively and positively charged ions (measured separately). The AIS detects particles between 0.8-40 nm and the BSMA between 0.8-7.5 nm in mobility diameter. BSMA has two parallel plate mobility analyzers, one for each polarity, and the particles are detected by depositing different-sized particles on a single detector plate by changing the voltage in the mobility analyzer. AIS has two cylindrical mobility analyzers, with the outer electrode consisting of insulated detector sections, which enables the simultaneous measurement of ions over the detected size range.

When used simultaneously, the DMPS and the ion spectrometers complement each other. While the AIS and the BSMA detect only naturally charged particles (which represent only a fraction of total particles), their advantage is the detection limits that extend down to the sizes where the nucleation takes place. Only during the recent years, instruments able to detect sub-3 nm neutral particles have been developed. These include Neutral Cluster and Air Ion Spectrometer (NAIS) (Asmi et al., 2009), which is a modified version of the AIS making use of chargers, and the advances in the CPC techniques (Iida et al., 2009; Vanhanen et al., 2011; Kuang et al., 2012).
2.2 Characterization of atmospheric new particle formation

2.2.1 New particle formation event classification

In studies on atmospheric NPF, event classification is utilized to analyze differences in ambient conditions between days with and without NPF and to provide a measure for the occurrence frequency of NPF. Over the years different classification schemes (e.g. Dal Maso et al., 2005; Hirsikko et al., 2007; Vana et al., 2008) have been used, however, in most of them the general idea is the same: days with clear NPF ('event'), days with no NPF ('non-event') and days with some signs of NPF but not a clear growing nucleation mode (e.g. 'undefined', 'featureless') are separated from each other by visual analysis of measured particle size distributions. The differences in classification schemes originate from differences in phenomena observed at different locations and in measurements with different instruments as well as from different focus points of the studies. In Paper I the modified classification scheme was developed by combining the schemes used previously in order to unify the NPF classification.

At K-puszta, a continental background site in Hungary, only one day was classified as non-event day and more than half of the days as event days during the 39 days long measurement period in May-June (Paper I). On the non-event day the condensation sink was higher than on average, but otherwise no clear difference separating the event, non-event and the other days from each other was found. This high event frequency was observed also later during one year of measurements at K-puszta (Manninen et al., 2010).

The over a decade long continuous aerosol particle size distribution measurements in Hyytiälä (SMEAR II station), a boreal forest background site in Southern Finland (Hari and Kulmala, 2005), have provided excellent characterization of NPF events. In Hyytiälä, on average, 24% of days are classified as NPF event days, and the event frequency peaks during spring and autumn (Dal Maso et al., 2005). Also in Hyytiälä, the condensation sink is typically lower on event days compared to non-event days, and events tend to occur during clear sky conditions (Lyubovtseva et al., 2005).
2.2.2 Formation and growth rate

New particle formation events are typically characterized by particle formation rate ($J$) and particle growth rate (GR). Formation rate is the number of new particles formed in a time interval (particles cm$^{-3}$ s$^{-1}$), and growth rate is the changing rate of the particle diameter (nm h$^{-1}$). Together $J$ and GR can be used for estimating the number of new particles that are formed, how many of them reach larger sizes and how fast this happens.

Particle formation rate is determined for some specific particle size, typically the lower detection limit of the instrument used (e.g. 3 nm or 10 nm for the DMPS), and describes the formation of particles larger than the size in question. These measured $J$ are smaller than the actual nucleation rate due to the coagulational losses during the growth, and, therefore, the measured $J$ should be corrected for these losses if the nucleation rate ($J_{nuc}$) is of interest (Kerminen and Kulmala, 2002).

For K-puszta (Paper I) the formation rate was determined from the DMPS measurements and calculated for 10 nm particles ($J_{10}$) due to the detection limit of the instrument. Due to the coagulational losses during the particle growth the corresponding formation rate of 3 nm particles ($J_{3}$), which is often reported in other studies, would be larger. The values of $J_{10}$ (median 1.2 cm$^{-3}$ s$^{-1}$) were within formation rate values typically observed in the atmosphere ($J_{3} = 0.01$-$10$ cm$^{-3}$ s$^{-1}$) (Kulmala et al., 2004c), however on the higher end of values for continental background sites and higher than the average in Hyytiälä ($J_{3} = 0.8$ cm$^{-3}$ s$^{-1}$) (Dal Maso et al., 2005).

The growth rates of particles during new particle formation are discussed in Sect. 3.
3 Atmospheric nanoparticle growth rates

3.1 Methods for determining particle growth rates

Growth of atmospheric nanoparticles during new particle formation events is typically studied based on particle size distribution measurements. In this thesis, measurements with DMPS (Paper I; Paper II), AIS (Paper I; Paper II) and BSMA (Paper II) were utilized for calculating nanoparticle growth rates, and two GR calculation methods called 'maximum concentration' and 'mode fitting' methods were used.

The ‘maximum concentration’ method (Paper I; Paper II; Lehtinen and Kulmala, 2003; Hirsikko et al., 2005) is based on finding the moments of time when the concentrations of particles of different sizes reach maximum (Fig. 2 a). A fitted Gaussian curve is often used for smoothing the fluctuations in measured data when determining the moments of maximum concentration. Due to the particle growth, the maximum concentration occurs first for the smallest particles and later for the larger ones, and GR is obtained by fitting a straight line to the data pairs of the moments of maximum concentration and particle diameter (Fig. 2 c). Typically, the line is fitted for size ranges of 1.5-3 nm, 3-7 nm and/or 7-20 nm in diameter (Fig. 2 c and d), depending on the detection limits of the instruments used (Paper I; Paper II; Hirsikko et al., 2005; Manninen et al., 2010). This allows for the analysis of the GR as a function of particle size.

The ‘mode fitting’ method (Paper II; Dal Maso et al., 2005) is based on following the time evolution of the average diameter of the nucleation mode particles. First, multi-modal log-normal size distribution is fitted to each momentarily measured particle size distribution to find the geometric mean diameter of the nucleation mode (Fig. 2 b) (Hussein et al., 2005). GR is then calculated by fitting a straight line to the data pairs of geometric mean diameter and time (Fig. 2 c). When using the ‘mode fitting’ method, typically only one line is fitted giving only one GR value for each NPF event (Paper I; Paper II; Dal Maso et al., 2005). In Paper II, the GR was calculated with the ‘mode fitting’ method for the size range 3-20 nm.

Both of these methods give an average changing rate of the diameters of the nucleation mode particles. In the absence of other processes, the calculated GR would equal the growth rate of the individual particles due to condensation of vapors. The main process interfering with the direct calculation of condensational growth rate is
Figure 2: Example of determining GR from measured particle size distributions. a) Concentration of 3.8 nm particles measured with the DMPS as a function of time (black dots) and a Gaussian curve (red line) fitted to find the time of maximum concentration (shown with the arrow). b) Particle size distribution measured with the DMPS at 12:38 (black dots) and the fitted modes (red line) used for finding the geometric mean diameter of the nucleation mode particles (shown with the arrow). c) Particle size distribution measured with the DMPS, the times of maximum concentration at each size section (blue markers), the mode geometric mean diameter as a function of time (black markers), and the lines fitted to these data points to find the GR (black line: fitted to mode average diameter in the range 3-20 nm; blue and magenta lines: fitted to the times of maximum concentration for size ranges 3-7 nm and 7-20 nm). d) Size distribution of negatively charged particles measured with AIS, the times of maximum concentration at each size section and the lines fitted to size ranges 1.5-3 nm, 3-7 nm and 7-20 nm. The measurements were performed in Hyytiälä on April 3rd 2004 and the time is expressed as local winter time.
coagulation. Both coagulational scavenging by larger pre-existing particles and self-coagulation within nucleation mode particles shape the particle size distribution and cause an increase in the average diameter. Typically, in rural areas, such as Hyytiälä, the apparent growth caused by coagulation has a minor effect (Leppä et al., 2011), however in polluted areas coagulation may affect the GR significantly (Stolzenburg et al., 2005). The ‘mode fitting’ method, as it is based on the shape of the particle size distribution, is more sensitive to coagulation and other size dependent processes compared to the ‘maximum concentration’ method. The ‘maximum concentration’ method is more sensitive to time dependent processes, e.g. air mass changes, than to size dependent processes. The advantage of the ‘maximum concentration’ method is its applicability to small sizes, where the cluster mode, visible in the smallest sizes in Fig. 2 d, may interfere with the mode fitting.

In Paper II, both GR calculation methods were applied for 3-20 nm particles using data measured with the DMPS. Typically, the ‘maximum concentration’ method gave a higher, on average 17 % higher, GR value than the ‘mode fitting’ method. The differences between the GRs calculated with the ‘maximum concentration’ method based on the measurements with the three instruments for > 3 nm particles were similar to those between the two GR calculation methods. For > 3 nm size range GRs based on the different instruments did not have systematic differences. For sub-3 nm size range, GRs calculated based on the AIS were on average higher than those calculated based on the BSMA, GRs calculated based on size distributions of negatively charged particles were on average lower than those calculated based on positively charged particles, and the uncertainty in GR related to the choice of instrumentation was 25 %. The difference between GRs calculated based on negatively and positively charged particle size distributions is expected to result from the changes in aerosol particle charging state and the earlier appearance of small negatively charged particles compared to positively charged particles during nucleation (Laakso et al., 2007a,b). Therefore, it likely does not indicate charge dependence in GRs. However, it does indicate the need for caution when size distributions of charged particles are used for representing total particle growth.

Several studies have utilized the ‘maximum concentration’ (e.g. Hirsikko et al., 2005; Manninen et al., 2010) and the ‘mode fitting’ (e.g. Dal Maso et al., 2005; Wehner et al., 2005) type of methods for studying nanoparticle growth. Other studies have calculated the GR based on, for example, the time lag between the rise of concentrations of sulfuric
acid and smallest detectable particles (Weber et al., 1997; Sihto et al., 2006), time lag between appearance of different sized particles (Kulmala et al., 2013) or charged fraction of particles (Iida et al., 2008). What is typical for many GR calculation methods applied to atmospheric particle size distribution data is that the size and time dependence of particle growth cannot be distinguished from each other. Some studies have suggested methods where size and time separation of GR is possible by fitting the aerosol general dynamic equation to the measured particle size distribution (Lehtinen et al., 2004; Verheggen and Mozurkewich, 2006; Kuang et al., 2012).

3.2 On theoretical constraints for condensational growth

Growth of aerosol particles by condensation occurs when gas phase partial pressure ($p_i$) of a condensing compound exceeds its equilibrium vapor pressure over the particle surface ($p_{eq,i}$). For particles much smaller than the mean free path of the condensing compound in the gas phase ($d_p << 60$ nm in atmosphere) GR due to the condensation of vapor $i$ can be written as (Fuchs and Sutugin, 1970; Lehtinen and Kulmala, 2003; Nieminen et al., 2010)

$$GR = \alpha_{m,i} \frac{(d_p + d_i)^2}{2d_p^2} \left( \frac{\tau_{p}^2}{c_i} + \frac{\tau_i^2}{c_p} \right)^{1/2} v_i (C_i - C_{eq,i})$$

(1)

where $\alpha_{m,i}$ is the mass accommodation coefficient, $d$ is diameter, $\tau$ is mean thermal speed, $v_i$ is molecular volume in condensed phase and subscripts $p$ and $i$ refer to the particle and the condensing vapor, respectively. The ambient molecular concentration ($C_i$) and equilibrium vapor concentration ($C_{eq,i}$) are connected to partial pressures $p_i$ and $p_{eq,i}$ through the ideal gas law $p = C k_B T$, where $k_B$ is Boltzmann constant and $T$ is temperature.

The equilibrium vapor pressure over particle surface depends on particle composition, size and the pure compound saturation vapor pressure according to (e.g. Seinfeld and Pandis, 2006)

$$p_{eq,i} = X_i \gamma_i(T, p, X_j)p_{sat,i}(T) \exp \left( \frac{4\sigma v_i}{k_B T d_p} \right)$$

(2)
where $X_i$ is particle phase molar fraction, $\gamma_i$ is activity coefficient, $p$ is total pressure, $p_{sat,i}$ is pure compound saturation vapor pressure, $\sigma$ is surface tension and $d_p$ is particle diameter. Activity coefficient $\gamma$ depends generally on the molar fractions of all the compounds $j$ in the particle. Product of $X_i$ and $\gamma_i$ is the activity term which depends on the composition of the particle, $p_{sat,i}$ is a property of the condensing compound and typically depends strongly on temperature ($p_{sat,i}$ increases with increasing $T$), and the exponent term is the Kelvin term which results from the curvature of the surface and increases strongly with decreasing particle size.

The condensational growth is driven by the difference between $p_i$ and $p_{eq,i}$. Assuming an effectively non-volatile vapor ($p_i >> p_{eq,i}$, $C_i >> C_{eq,i}$) Eq. (1) indicates that GR decreases with increasing particle size (magenta line in Fig. 3). Assuming further the thermal movement of the particle ($c_p$) and size of the condensing molecule ($d_i$) to be negligible, Eq. (1) reduces to the equation 8 in Paper II (there is a typo in the equation 8 in Paper II: the factor in denominator should be 2) and leads to constant GR as a function of $d_p$. On the other hand, when the $C_{eq,i}$ is not negligible compared to $C_i$ the difference $C_i - C_{eq,i}$ increases with increasing particle size and, as a result, GR increases with the particle size (Fig. 3). This is due to the Kelvin term which can increase the $p_{eq}$ by one or even several orders of magnitude (depending on the $\sigma$ and $v_i$) for 1.5 nm particles compared to 20 nm particles.

3.3 Observations of the atmospheric nanoparticle growth rates

Growth rates of nucleation mode particles reported for various atmospheric environments vary typically between 1-20 nm h$^{-1}$ (Paper II; Kulmala et al., 2004c, and references therein). However, lower GRs on the order of 0.1 nm h$^{-1}$ have been observed occasionally at several locations (Kulmala et al., 2004c), including boreal forest (Paper II), high elevation (Asmi et al., 2011; Neitola et al., 2011), remote coastal (Modini et al., 2009) and subarctic (Svenningsson et al., 2008), as well as urban (Wu et al., 2007) sites. Also higher GRs, reaching values of several tens of nanometers per hour, have been measured e.g. at boreal forest (Paper II), remote coastal (Modini et al., 2009) and subarctic (Svenningsson et al., 2008), semi-clean savannah (Vakkari et al., 2011) and urban (Iida et al., 2008) sites. Therefore, although the average GRs for different sites are within one order of magnitude, the variation in GR values measured
Figure 3: Growth rate as a function of particle size calculated according to Eq. (1) for gas phase concentration $C = 10^8$ cm$^{-3}$ ($\approx 4 \cdot 10^{-7}$ Pa) and four different saturation vapor pressures $p_{sat}$. Other properties were as for Organic acid 1 in paper IV (molar mass 104 g mol$^{-1}$, density 1500 kg m$^{-3}$ and surface tension 30 mN m$^{-1}$).

at a same location extends in some cases even over two orders of magnitude.

Nanoparticle GRs increase with particle size at many locations, at least on average (Paper I; Paper II; Fiedler et al., 2005; Virkkula et al., 2007; Suni et al., 2008; Modini et al., 2009; Manninen et al., 2010; Vakkari et al., 2011; Kulmala et al., 2013), although not in all environments (Fiedler et al., 2005; Manninen et al., 2010). These observations are often based on GR calculation methods where time and size dependences cannot be distinguished from each other, and, thus, the apparent size dependence could be in reality, at least partly, time dependence. Since the growth rate of the larger particles is calculated based on later moment in time, the GRs of different size particles may correspond to different ambient conditions. This is illustrated in Fig. 4 where the ambient conditions are averaged over the time period of growth rate calculation of each size range for summertime NPF events. On the other hand, Kuang et al. (2012), with their GR calculation method where size and time dependence can be distinguished, observed that GR of sub-5 nm particles changes both with time and particle size.

The vapors participating in particle nucleation are expected to contribute also to the
Figure 4: Particle growth rates as a function of particle diameter and temperature, UVB radiation intensity and sulfuric acid concentration ('proxy' calculated as described in Paper II based on Petäjä et al. (2009)) during the time period when GR in different size ranges was calculated. Averages over summertime (June-August) NPF events in Hyytiälä during 2003-2009.

subsequent condensational growth. However, although sulfuric acid seems to drive the nucleation of atmospheric nanoparticles, it does not seem to be the key compound for the subsequent growth: in many environments, based on its gas phase concentration, condensation of sulfuric acid, accompanied by neutralization by ammonia, can explain only some percents or tens of percents of observed GRs (Weber et al., 1997; Birmili et al., 2003; Kulmala et al., 2004c; Boy et al., 2005; Fiedler et al., 2005; Stolzenburg et al., 2005; Kuang et al., 2010; Riipinen et al., 2011; Kuang et al., 2012). The rest of the growth is expected to be mostly due to organic vapors (Kulmala et al., 2004c; Kulmala and Kerminen, 2008). The significant role of organic compounds on the nanoparticle growth is supported by measurements of chemical composition of nucleation mode particles (O’Dowd et al., 2002; Smith et al., 2008; Riipinen et al., 2009; Smith et al., 2010; Laitinen et al., 2011; Bzdek et al., 2012), but also by the observations of the nanoparticle GR. Further, while the relative contribution of sulfuric acid is reported to decrease with increasing particle size, typically condensation of sulfuric acid does not explain even the GR of the sub-3 nm particles (Fiedler et al., 2005; Riipinen et al., 2011; Kuang et al., 2012). This implies that organics have an important role in the growth starting from the first steps. In some locations, typically in polluted environments, sulfuric acid can, however, explain most or all of the condensational growth (Birmili et al., 2003; Stolzenburg et al., 2005; Yue et al., 2010), indicating that the processes and compounds driving the nanoparticle growth vary in the atmosphere.
The observed size dependence of GR supports the importance of organic compounds in nanoparticle growth and can be explained by the properties of these compounds (Kulmala et al., 2004b). Oxidation of VOCs produces a large variety of compounds with varying saturation vapor pressures, some of which (i.e. highly oxidized compounds such as high molecular weight dicarboxylic acids) have low enough saturation vapor pressures to condense on aerosol particles at atmospheric conditions (see Sect. 4). Their saturation vapor pressures are, however, typically higher than that of sulfuric acid, and, therefore, their condensation on the smallest particles is reduced or even suppressed by the Kelvin effect – leading to increase in GR as a function of the particle size in two ways. First, increase in particle size lowers the equilibrium vapor pressure and increases the driving force \( C_i - C_{eq,i} \) of condensation for each vapor as discussed in Sect. 3.2 and shown in Fig. 3 (Kulmala et al., 2004b). Second, as the particle size increases and Kelvin term decreases, compounds with higher \( p_{sat} \) can start condensing on the particle (as seen by comparing the starting points of black, blue and red lines in Fig. 3). This increases GR because more of the compounds are contributing to the growth. Also, concentrations of these higher \( p_{sat} \) oxidation products are likely to be higher compared to the lowest \( p_{sat} \) compounds, which further increases the GR with particle size (Winkler et al., 2012). The equilibrium vapor pressure depends also on the composition of the particle and is lower in case of a multi-component particle compared to a pure one-compound particle. Therefore, an organic compound can activate with respect to condensation on a multi-component particle at lower gas phase concentration than at which a pure compound particle would grow – a phenomenon referred to as Nano-Köhler theory in analogy to Köhler theory for water droplets (Kulmala et al., 2004a).

At a boreal forest site in Hyytiälä the observations of the GRs over seven years confirmed that the GRs of particles > 3 nm have a clear seasonal cycle with maximum occurring during summer, while the GRs of sub-3 nm particles are rather invariant throughout the year (Fig. 5) (Paper II; Dal Maso et al., 2005; Hirsikko et al., 2005). In the winter time the GRs are similar for all size ranges, but towards the summer the GRs of different sized particles start to deviate from each other, and during summer a clear size dependence was observed. These differences in GRs between season and particle size are larger than what could be explained by the uncertainties in the GR calculation method or by coagulation (Sect. 3.1), and are, thus, caused by properties or abundances of the condensing vapors.
Figure 5: Monthly median GRs at Hyytiälä averaged over seven years. The whiskers represent the 10th and 90th percentiles. Figure reproduced from Paper II.

The observed GRs in Hyytiälä, where the ambient conditions are expected to be greatly affected by the emissions of biogenic organic vapors, strongly point towards the importance of biogenic organic trace gases on nanoparticle growth. The seasonal variation of > 3 nm particle GRs is similar to the seasonal variation of biogenic organic trace gas concentrations – which is distinctly different from that of sulfuric acid concentration, NPF event frequency and particle formation rate (Dal Maso et al., 2005). This indicates that the organic vapors, rather than sulfuric acid, are likely to control the seasonal cycle of GRs of > 3 nm particles, and that the particle growth is limited by different processes than those controlling the nucleation. Highest GRs during summer imply that the growth of the > 3 nm particles is limited more by the abundance of the condensing vapors than by their saturation vapor pressures which increase strongly with increasing temperature. Further, the comparison of GRs of > 3 nm particles with ambient conditions suggests that the concentrations of volatile organic precursor gases are at least as important as a limiting factor for the growth as their oxidation. This is presumably because NPF events take place predominantly on days with clear sky (Lyubovtseva et al., 2005) when oxidation is not limited by the UVB radiation intensity.

The controlling factors for growth of < 3 nm particles in Hyytiälä are more uncertain. They are rather constant throughout the year and even < 3 nm particle growth can
not be explained by sulfuric acid (Riipinen et al., 2011; Kulmala et al., 2013). One possible explanation for the lack of summer maximum in GRs of < 3 nm particles is the increase in saturation vapor pressure with temperature. Since the growth-limiting effect of equilibrium vapor pressure is strongest for these smallest particles, the temperature dependence of saturation vapor pressure may prevent the increase of GR even though concentrations of condensing vapors are higher during summer.

Also at the K-puszta measurement site GR increased with particle size during a large fraction of the NPF events, on average from 1.7 nm h\(^{-1}\) for sub-3 nm particles to 6.1 nm h\(^{-1}\) for 10-20 nm particles (Paper I). The study presented in Paper I was based on a short measurement campaign lasting 39 days in May-June, and, therefore, it was not possible to investigate the seasonal variation of GR at this site. The GR values reported in Paper I are rather similar to those observed later during one year of measurements at K-puszta (Manninen et al., 2010). However, when calculated based on the one year of measurements (Manninen et al., 2010), the average GR of sub-3 nm particles was twice as high compared to the shorter campaign. This underlines the need for long measurement campaigns in characterizing new particle formation for different environments. No notable correlation was found between GR and meteorological parameters or trace gas concentrations. However, GRs were higher during the latter part of the campaign which corresponds to the warm period with continental air masses and higher concentrations of many of the trace gases, including monoterpenes, isoprene and SO\(_2\), compared to the first half of the campaign. Therefore, the driving factor for the growth may have been monoterpane oxidation products, however the evidence for this is not clear.
4 Uptake of organic compounds by nanoparticles

4.1 Formation of semi- and low-volatile organic material

Semi- (exists in both gas and particle phase at equilibrium) and low-volatile (exists mostly in the particle phase at equilibrium) organic compounds are formed in the oxidation of VOCs, which can take place in the gas phase, at the particle surface and/or in the particle phase (Kroll and Seinfeld, 2008; Hallquist et al., 2009; Kroll et al., 2011). The most important source for SOA formation is the oxidation of monoterpenes (Hallquist et al., 2009). VOCs are oxidized in the atmosphere by hydroxyl (OH) and nitrate (NO$_3$) radicals and by ozone (O$_3$) (Kroll and Seinfeld, 2008). Upon oxidation, the organic compounds may gain functional groups (functionalization), fragment into smaller molecules (due to cleavage of C-C bonds) or form oligomers (Kroll and Seinfeld, 2008; Jimenez et al., 2009; Kroll et al., 2011). First generation oxidation products of VOCs may not necessarily form SOA, and further oxidation is needed (Jimenez et al., 2009). Therefore the oxidation of VOCs produces a large variety of compounds with varying volatility, and only part of the produced compounds have a low enough volatility to partition in the particle phase in substantial amounts (Kroll and Seinfeld, 2008; Jimenez et al., 2009; Kroll et al., 2011).

In addition to oxidized hydrocarbons, another group of interest are amines (ammonia with one or more H substituted with an organic group). Amines are emitted into the atmosphere, for example, from anthropogenic sources, vegetation and oceans, and they have been detected in the atmosphere in both gas and particle phase (Ge et al., 2011a). Most abundant amines in the atmosphere are low molecular weight aliphatic amines, such as dimethylamine (DMA) (Ge et al., 2011a), which, based on their high saturation vapor pressures, would not be expected to exist in particle phase (Ge et al., 2011b). However, their saturation vapor pressure can be reduced by gas phase oxidation, and, more importantly, aliphatic amines are strong bases and highly water soluble and can, therefore, partition in the particle phase by taking part in acid-base chemistry and by dissolving in aqueous particle phase (Murphy et al., 2007; Ge et al., 2011b). Due to their expected importance in nucleation (Kurtén et al., 2008), amines are also of interest with respect to nanoparticle growth.

Based on the observed atmospheric GRs and estimations of atmospheric organic material concentrations, the saturation vapor pressures of the compounds growing atmo-
Volatile organic compounds (VOC) form semi- and low-volatile compounds through gas phase oxidation. These compounds partition in the particle phase where they may be further transformed into less volatile species.

Spheric nanoparticles should be on the order of $10^{-8}$-$10^{-7}$ Pa (corresponds approximately to $10^{-8}$-$10^{-2}$ µg m$^{-3}$ and $10^6$-$10^7$ cm$^{-3}$) or lower (Kulmala et al., 1998; Pierce et al., 2011; Donahue et al., 2011). Compounds with such low saturation vapor pressures may be either formed in the gas phase or the volatility of the compounds can be further reduced in condensed phase. Therefore, mechanisms of nanoparticle growth by organics can be roughly divided into two: (1) production of semi- and low-volatile organic vapors by gas phase oxidation and vapor pressure driven condensation, and (2) reactive uptake, i.e. transformation of condensing compounds into less volatile ones through particle phase or surface reactions (Fig. 6) (Rudich et al., 2007; Hallquist et al., 2009).

Saturation vapor pressure typically decreases with increasing molecular weight and addition of polar functional groups (such as carboxylic acid (-COOH) and hydroxyl (-OH) groups) (Pankow and Asher, 2008). Therefore, the gain of oxygen containing functional groups or oligomerization upon oxidation likely lead to the formation of lower $p_{sat}$ compounds. Oligomerization is more likely to take place in particle phase than in the gas phase (Kroll and Seinfeld, 2008), and, thus, vapor pressure driven condensation is expected to be mainly due to condensation of highly oxidized (high O:C ratio) gas phase oxidation products with oxygen containing functional groups. While
only the most oxidized organic compounds identified in the atmosphere have saturation vapor pressures low enough to grow the nanoparticles through vapor pressure driven condensation (Goldstein and Galbally, 2007), increasing interest has focused on reactive uptake.

Reactive uptake can take place in multiple ways. Oligomerization of organics can take place in particle phase or at the particle surface, e.g. due to reactions with ozone through formation of Criegee intermediates (Zhang and Wexler, 2002; Rudich et al., 2007; Kroll and Seinfeld, 2008) or catalyzed by the acidity of the particle (Wang et al., 2010; Limbeck et al., 2003; Zhang and Wexler, 2002). Since the nucleated particles likely contain sulfuric acid, the formation of organosulfates, which are expected to have low saturation vapor pressure, (Zhang and Wexler, 2002; Surratt et al., 2007) or the neutralization of sulfuric acid by amines (Wang et al., 2010) could account for the first steps of the nanoparticle growth. Further, short chain organic acids and aliphatic amines, which have saturation vapor pressures higher than those required for significant vapor pressure driven condensation, have been observed in atmospheric nanoparticles (Smith et al., 2008, 2010; Laitinen et al., 2011). This observation has been speculated to indicate that salt formation could be enhancing the condensation of not only amines, but also organic acids (Barsanti et al., 2009). The effect of salt formation is that the dissociation of acids (loss of H) and protonation of bases (gain of H) produces either salt ions or crystal salt, both of which are less likely to evaporate from the particles than the parent acids and bases.

In Paper III the various pathways to SOA formation were investigated based on their importance in the nanoparticle growth (Box 1 in Paper III). For the growth of the smallest, 1-5 nm, particles the condensation of nucleating vapors and acid-base chemistry is expected to be important (Zhang and Wexler, 2002; Smith et al., 2008; Barsanti et al., 2009; Wang et al., 2010; Smith et al., 2010). Also, vapor pressure driven condensation of gas-phase oxidation products is likely to contribute, although the net flux towards particles is considerably restricted by the surface curvature effect on equilibrium vapor pressures. OH is often assumed to be the most important oxidant for SOA formation (Donahue et al., 2012), and laboratory experiments suggest OH to be the main oxidant for the first steps of growth, while O_3 oxidation would become more important as the particles get larger (Hao et al., 2009).

As the particles grow further, the relative importance of different processes is likely to change. The vapor pressure driven condensation is enhanced as the surface curva-
The role of salt formation (dissociation of acids and protonation of bases) in nanoparticle growth was studied in this thesis utilizing two nanoparticle growth models (Paper II and III). Salt formation can significantly affect the equilibrium vapor pressure of particles, which in turn influences the growth of nanoparticles. Field observations have shown that organic salts can account for 23-47% of the particle growth (Smith et al., 2010), and laboratory experiments indicate that oligomerization may also play a role in smaller size ranges (Wang et al., 2010). On the other hand, for particles larger than 20 nm, there is no evidence of salt formation having a significant role in particle growth, while significant contributions of oligomers, even >50% by mass, have been observed in laboratory experiments (Kalberer et al., 2004; Heaton et al., 2007; Hall and Johnston, 2011).

The physical phase of particles also affects the uptake of vapors through the effects on saturation vapor pressure, diffusional mixing, and chemical reactions. The typical assumption of SOA being liquid particles may cause uncertainty in model predictions (Rudich et al., 2007; Shiraiwa et al., 2011; Vaden et al., 2011). Atmospheric nanoparticles have been observed to have similar bouncing properties as amorphous particles, and the resemblance to amorphous phase increases with particle size suggesting that nucleated particles might initially be liquid and go through a phase change to amorphous phase during the growth (Virtanen et al., 2010, 2011). The mixing timescales depend on particle size, estimates being on the order of seconds, minutes, and hours for 5, 20, and 50 nm particles (Paper III; Shiraiwa et al., 2011). Therefore, mixing is probably a minor issue for the growth of <20 nm particles, but it might affect the growth of larger particles.

It should be noted that the abovementioned estimates of importance of different processes are associated with uncertainty due to the lack of identification of the organic compounds and knowledge of their properties. Further, laboratory studies are often performed with higher precursor concentrations and mass loadings compared to atmospheric conditions and in shorter time scales compared to atmospheric nanoparticle growth, which may affect the gas-particle partitioning (Presto and Donahue, 2006; Rudich et al., 2007; Pankow and Chang, 2008; Shilling et al., 2009; Gao et al., 2010), and the observations of the atmospheric nanoparticle composition are still infrequent.

4.2 Role of salt formation in atmospheric nanoparticle growth

The role of salt formation (dissociation of acids and protonation of bases) in nanoparticle growth was studied in this thesis utilizing two nanoparticle growth models (Paper
Both models predict the evolution of the particle size and composition based on the gas phase concentrations of the condensing vapors and the initial particle size and composition. The growth of atmospheric nanoparticles, especially in boreal forest region, was studied, and based on the observations of Smith et al. (2010) a system with sulfuric acid, one organic acid, ammonia and one amine as the condensing vapors was modeled (Fig. 7). In calculations with one of the models, MABNAG, the condensation of water was also included. Both models are currently set to calculate the growth of monodisperse particle population.

One of the models, MABNAG, utilizes detailed thermodynamics for calculations of the particle phase acid-base chemistry, and the other model estimates the salt formation based on the stabilities of molecular clusters. Therefore, in the former the salt formation is calculated based on the bulk properties, while the latter approach relies on the properties of clusters of only few molecules.

4.2.1 Model for acid-base chemistry in nanoparticle growth (MABNAG)

MABNAG (Model for Acid-Base chemistry in NAnoparticle Growth) is a particle growth model where the dynamics of condensation and evaporation of vapors to/from particles have been combined with the thermodynamics of particle phase acid-base chemistry (Paper IV). Although dissociation of organic acids is included in some previous models (Couvidat et al., 2012; Tost and Pringle, 2012), the detailed thermodynamics of acid-base chemistry involving both organic acids and bases together with inorganic compounds were for the first time applied for nanoparticle growth in MABNAG.

Current version of MABNAG assumes the particles to be aqueous solution aerosol particles, and the condensing vapors can include both inorganic and organic compounds in addition to water. The aim in Paper IV was to make an upper limit estimation for the role of salt formation in the nanoparticle growth, and the assumptions in MABNAG model were made accordingly.

The condensation of the acids is calculated in MABNAG based on their mass fluxes towards a particle (Fuchs and Sutugin, 1970; Vesala et al., 1997; Lehtinen and Kulmala, 2003)

\[
\frac{dm_i}{dt} = \frac{2\pi (d_p + d_i)(D_p + D_i) \beta_{m,i} M_i}{RT} \left(p_i - p_{eq,i}\right)
\]
Figure 7: Systems studied with a) MABNAG and b) the growth model where salt formation is accounted for based on the stabilities of molecular clusters. Part a) reproduced from Paper IV.
where $m$ is particle phase mass, $d$ is diameter, $D$ is diffusion coefficient, $M$ is molar mass, $R$ is general gas constant, $T$ is temperature, $p_i$ is ambient partial pressure of $i$, $p_{eq,i}$ is equilibrium vapor pressure of $i$ over the particle surface, and subscripts $i$ and $p$ refer, respectively, to the vapor (sulfuric acid or organic acid) and to the particle. Equation (3) has the form of the continuum regime mass flux, and the transition regime correction factor $\beta_{m,i}$ accounts for the deviance from continuum situation when the particle size is comparable to or smaller than the mean free path of the condensing vapor molecules $i$. The transition regime correction factor is calculated according to (Fuchs and Sutugin, 1970)

$$
\beta_{m,i} = \frac{1 + Kn_i}{1 + \left(\frac{4}{3 \alpha_{m,i}} + 0.377\right) Kn_i + \frac{4}{3 \alpha_{m,i}} Kn_i^2}
$$

(4)

where $Kn_i$ is the Knudsen number, which describes the length of the vapor mean free path relative to the particle size, and $\alpha_{m,i}$ is the mass accommodation coefficient. Diffusional movement of the particles and the dimension of the vapor molecule are taken into account when calculating the Knudsen number

$$
Kn_i = \frac{2 \lambda_i}{d_p + d_i}
$$

(5)

and the vapor molecule mean free path $\lambda_i$

$$
\lambda_i = \frac{3 (D_p + D_i)}{(\bar{c}_p^2 + \bar{c}_i^2)^{1/2}}
$$

(6)

where $\bar{c}_p$ and $\bar{c}_i$ are the mean thermal speeds of the particle and vapor molecule $i$, respectively.

In the version of MABNAG used in Paper IV, bases and water were assumed to constantly instantaneously equilibrate between gas and particle phase. Therefore, the mass of bases and water in a particle were calculated maintaining the equilibrium

$$
p_{eq,i} = p_i
$$

(7)
for them during the particle growth. This assumption is based on the shorter diffusion timescales of the considered bases and water compared to the acids, but it might somewhat overestimate the partitioning to the particle phase especially for the amine (Paper IV).

For all of the compounds, regardless of whether Eq. (3) or Eq. (7) was used, the contribution to the particle mass was affected by their ambient vapor pressures and their equilibrium vapor pressures. For the equilibrium vapor pressures, MABNAG considers both the size and the composition dependency (Eq. (2)).

In the particle phase, the acid-base chemistry is included, which means accounting for the dissociation of acids and protonation of bases. To calculate the composition dependence of $p_{eq}$ and the particle phase acid-base chemistry, the growth dynamics part of MABNAG is coupled to Extended Aerosol Inorganics Model (E-AIM; Clegg et al., 1992; Wexler and Clegg, 2002; Clegg and Seinfeld, 2006a,b). Since E-AIM is a thermodynamic equilibrium model, the particle phase is assumed to be constantly in equilibrium with respect to the acid-base chemistry during the particle growth.

E-AIM includes only dissociation chemistry, and no other chemical reactions are taken into account. In E-AIM, the first dissociation of sulfuric acid ($\text{H}_2\text{SO}_4 \rightarrow \text{HSO}_4^- + \text{H}^+$) is always assumed to be complete in the aqueous phase. The second dissociation of sulfuric acid ($\text{HSO}_4^- \rightarrow \text{SO}_4^{2-} + \text{H}^+$) and the dissociation/protonation of the other compounds are calculated based on the dissociation constants. As the dissociation of water was also allowed, there were in total 12 particle phase species included in the calculations for the system modeled in Paper IV (Fig. 7). The activity coefficients of the solutes are calculated based on purely organic and inorganic aqueous solutions with same molality as in the mixture. Activity (product of $X_i$ and $\gamma_i$ in Eq. (2)) of water is calculated as the product of the water activities in the purely organic and inorganic aqueous solutions to account for the effects of all the solutes (Clegg and Seinfeld, 2006a; Clegg et al., 2001).

4.2.2 Growth model with salt formation included based on stabilities of molecular clusters

In Paper III nanoparticle growth was studied with a model were the particle phase salt formation was included on a conceptual basis rather than applying the full thermody-
namics of acid-base chemistry (here called ‘conceptual model’). The changes of particle phase mass of each of the compounds was calculated based on their mass fluxes (Eq. 3). For the acids, the equilibrium vapor pressures were calculated assuming an ideal mixture, i.e. $\gamma_i = 1$ in Eq. (2), and $\alpha_{m,i}$ was set to unity. For the bases, the equilibrium vapor pressure was set to zero and the evaporative flux was taken into account using effective mass accommodation coefficients $\alpha_{m,eff,i}$ calculated as a product of $\alpha_{m,i}$ and acid mole fraction. For these the $\alpha_{m,i}$ for bases were estimated based on quantum chemistry calculations of evaporation of small molecular clusters (Kurtén et al., 2008), and values $\alpha_{m,amine} = 1$ and $\alpha_{m,ammonia} = 0.001$ were used, respectively, for amine (estimated based on DMA) and ammonia. The ratio $\alpha_{m,amine}/\alpha_{m,ammonia}$ reflects the relative basicity of these compounds.

In the particle phase the acids we allowed to exist in their neutral form or as salts formed with one of the bases in 1:1 molar ratio. The bases were allowed to exist in particles only as salts formed with the acids, and the excess bases were assumed to evaporate immediately from the particle. Therefore, the particle phase had six compounds: two acids and four salts formed from one acid and one base (Fig. 7b). The effective mass accommodation coefficients were also used for estimating the relative strengths of the ammonium and aminium salts, and the bases were assigned to the four salts based on their $\alpha_{m,eff}$ and the molar fractions of the two acids.

### 4.2.3 Model predictions for the role of salt formation in nanoparticle growth

In Paper IV MABNAG model was used for studying the role of salt formation in nanoparticle growth at varying ambient conditions, with a special focus being on the boreal forest environment. Especially, the effect of acid-base chemistry on the condensation of organic acids and the relative roles of the two bases (ammonia and amine) were explored. The organic acid was a short chain dicarboxylic acid (malonic acid) in line with the observations by Smith et al. (2010), and the DMA was selected to present all the low molecular weight amines in order to make an upper limit estimate for the organic salt formation.

The results indicate that in the considered system of condensing vapors the different compounds affect each others partitioning to the particle phase through acid-base chemistry. For typical ambient conditions in Hyytiälä, MABNAG predicted only a small
Figure 8: Dissociated fraction of particle phase organic acid at particle sizes a) 3 nm, b) 7 nm and c) 20 nm as a function of ammonia concentration for three amine concentrations predicted with MABNAG. Concentration and saturation vapor pressure of organic acid were set to $3 \cdot 10^8$ cm$^{-3}$ and $10^{-6}$ Pa. Other properties of the organic acid were as for Organic acid 1 (Table 1 in Paper IV). Sulfuric acid concentration ($10^6$ cm$^{-3}$), RH (40 %) and temperature (283.15 K) were set to base case values in all simulations (Table 2 in Paper IV). Figure reproduced from Paper IV.

fraction (< 10 %) of particle phase organic acid to dissociate (Fig. 8). Consequently, a rather low saturation vapor pressure, $10^{-6}$ Pa, was required for reaching atmospheric growth rates. On the other hand, the dissociated fraction of the organic acid depended strongly on the concentrations of the bases, and at elevated base concentrations significant fraction (20-90 %) of organic acid was predicted to dissociate increasing the mass flux of the organic acid towards the particle. Since the condensation of organic acid accounted for most of the particle mass, the increased dissociation was reflected in the particle growth rates: with elevated base concentrations the GR increased more than what can be explained by only the increased contribution of bases in the particle mass. Further, the competition of the bases between the acids is seen in the increase of dissociated fraction of organic acid with particle size as relative contribution of sulfuric acid decreases.
All the particle phase ammonia and amine were predicted to be in their protonated form in particle phase. This together with the dissociation of sulfuric acid led to 11-50% of particle mass being formed from the salts at typical condition for Hyytiälä despite of the small dissociated fraction of the organic acid. Due to the increase in the mass fraction of organic acid, the salt mass fraction decreased with increasing particle size. The relative contributions of the two bases were rather similar for all particle sizes and strongly dependent on their gas phase concentrations: ammonia was a more important base if its gas phase concentration was at least one order of magnitude higher than that of amine, otherwise amine was more important. Thus, the typical conditions in Hyytiälä (Paper IV, Appendix A) are on this border, making it important to include both ammonia and amines in the calculations.

The short chain carboxylic and dicarboxylic acids detected in the nanoparticles in Hyytiälä using Thermal Desorption Chemical Ionization Mass Spectrometer (TD-CIMS) (Smith et al., 2010) have higher saturation vapor pressures than required in MABNAG to reach the atmospheric growth rates with reasonable assumptions of the gas phase concentrations. Since MABNAG predictions were not sensitive to the assumed dissociation constant of the organic acid, based on MABNAG those organic acids would not be expected to exist in nanoparticles in significant amounts except in high-base conditions. The model predictions, therefore, disagree with the measurements. One can speculate about the measurement uncertainties and other processes, such as oligomerization or organosulfate formation, being involved, as well as about the uncertainties in the thermodynamic properties used in the model. For example, the results from Paper V suggest that the current thermodynamic model might overestimate the volatility of organic acids in case of a mixed organic/inorganic particles when the particle is mostly inorganic. Therefore, the condensation of the organic acid might be underestimated in MABNAG at the smallest sizes where molar fraction of inorganic compounds is higher compared to the organic acid. However, it is also worth noting that the acid-base chemistry in the model is based on bulk thermodynamics, and such approach might not fully capture the behavior of the nanometer sized particles. Therefore, it is interesting to compare MABNAG to the growth model where salt formation was estimated based on cluster stabilities.

MABNAG and the conceptual model where salt formation was included based on the cluster stabilities agree qualitatively on the contribution of the two acids (Fig. 9 a and b): at typical ambient conditions for boreal forest site Hyytiälä (for details, see Paper
IV) both models predict the dry mass fraction of sulfuric acid to decrease rapidly, and the dry mass fraction of the organic acid to increase as the particle grows. According to both of the models, sulfuric acid accounts for only less than 5 % and organic acid more than 60 % of the increase in the particle dry mass when the diameter reaches 10 nm. Both models also predict the particle composition to stay rather constant after 10-20 nm. However, the two models disagree regarding the bases: compared to MABNAG, the conceptual model predicts much larger mass contribution for the amine and smaller contribution for ammonia. The maximum dry mass fraction of amine at about 1.1 nm results from the initial composition assumption (4 sulfuric acid and 2 amine molecules), but the clearly larger contribution of amine predicted with the conceptual model above 2 nm is not affected by this assumption. The larger contribution of amine and the assumption of equal stabilities of the salts formed from sulfuric acid and organic acid (equal strength as acids) together resulted in a larger fraction of organic acid being dissociated according to the conceptual model compared to MABNAG (Fig. 9 c). The latter affects the dissociation below 5 nm (due to the significant contribution of sulfuric acid), and above 5 nm the former is the main cause. The higher contribution of amine and the enhanced dissociation of organic acid together caused the particle growth to be much faster according to the conceptual model compare to MABNAG (Fig. 9 d).

The difference in predictions between the two models reflects the challenges in modeling the nanoparticle size scale where neither bulk thermodynamics (which MABNAG is based on) nor the molecular scale quantum chemistry (which was made use of in the conceptual model) might be directly applicable. The conceptual model type of approach is more likely to capture the initial steps of growth of particles when they are clusters of only small number of molecules. As the particles grow above 2-3 nm the number of molecules in a particle increases fast, and models like MABNAG become more reliable.
Figure 9: Predicted particle phase dry mass fractions as a function of particle diameter according to a) MABNAG and b) the growth model where salt formation is accounted for based on cluster stabilities (Conceptual model), c) dissociated fraction of organic acid as a function of particle diameter, and d) particle diameter as a function of time. In a) and b) the neutral form and dissociation/protonation products are summed up for each acid/base. Gas phase concentrations were as follows: sulfuric acid $10^{-6}$ cm$^{-3}$, organic acid $3 \cdot 10^{-6}$ cm$^{-3}$, ammonia $10^{-9}$ cm$^{-3}$ and amine $10^{-9}$ cm$^{-3}$. RH was 40 % (for MABNAG) and temperature was 283 K. Properties of Organic acid 1 and DMA from table 1 in Paper IV were used.
5 Volatility of organic aerosol constituents in the presence of inorganic salt

Atmospheric aerosol particles are complex mixtures of organic and inorganic compounds, and the particle composition is likely to affect the gas-particle partitioning. Equilibrium vapor pressure is an important property determining the partitioning of compounds between gas and particle phase, and its variation with temperature and particle composition needs to be known to capture SOA formation and nanoparticle growth in models (Donahue et al., 2006; Pankow and Chang, 2008). It is unrealistic to expect to find these dependencies for equilibrium vapor pressures of all the thousands of atmospheric organic compounds (Goldstein and Galbally, 2007), but detailed studies of the properties of some example compounds bring valuable information about the atmospheric SOA formation.

Even if a compound that condenses on a particle would not go through particle phase chemical reactions, its equilibrium vapor pressure and, therefore, the tendency to evaporate can be affected by interactions with other particle phase constituents. Mathematically the effect of interactions between the particle phase species is described by the activity coefficient ($\gamma$ in Eq. (2)). Parameterizations of activity coefficients can be obtained directly from measurements of particular, typically aqueous, mixtures (e.g. Redlich and Kister, 1948) or be estimated based on group contribution methods, e.g. UNIFAC (Fredenslund et al., 1975). These parameterizations are typically developed based on measurements of water activity, from where the solute activity can be derived. However, their performance in predicting the composition dependence of equilibrium vapor pressures of the solutes is seldomly tested.

Dicarboxylic acids (organic acids with two carboxylic acid groups -COOH) are among the organic compounds with lowest saturation vapor pressures that are identified in the atmosphere, and based on their saturation vapor pressures they are classified as semi- or low-volatile (Goldstein and Galbally, 2007). They are often found in the atmospheric aerosol particles (Kawamura and Ikushima, 1993; Kawamura et al., 1996; Kerminen et al., 2000), also in the nanoparticles (Smith et al., 2010; Laitinen et al., 2011). Pure compound saturation vapor pressures of straight chain dicarboxylic acids have been the topic of a number of studies (e.g. Bilde et al., 2003; Koponen et al., 2007; Cappa et al., 2007; Booth et al., 2010), but the effect of inorganic particulate constituents on their volatility in mixed particles has been studied less. Studies of
the hygroscopicity of particles containing mixtures of dicarboxylic acids, or their salts, and inorganic salts have been conducted (Bilde and Svenningsson, 2004; Clegg and Seinfeld, 2006a; Hanford et al., 2008; Pope et al., 2010a; Wu et al., 2011), but the effect of inorganic salts on the volatility of the dicarboxylic acids has been subject of only three studies so far (Paper V; Pope et al., 2010b; Zardini et al., 2010).

In Paper V, the possible effect of inorganic salt on the evaporation of organic acid was studied based on laboratory experiments of evaporation of aqueous solution droplets, and the experimental results were interpreted using a theoretical evaporation model. The droplets contained succinic acid (HOOC(CH$_2$)$_2$COOH) as the organic acid and ammonium sulfate ((NH$_4$)$_2$SO$_4$) as the inorganic salt.

5.1 Laminar flow tube experiments

The experiments were performed at the University of Copenhagen using a Tandem Differential Mobility Analyzer setup (TDMA) (Koponen et al., 2007) for monitoring size changes of sub-micron aqueous solution droplets during their evaporation. A nearly monodisperse population of droplets generated by atomizing a liquid solution was selected with a mobility analyzer and led to a 3.5 m long laminar flow tube which provided evaporation times of up to few minutes. The droplet size was measured with a Scanning Mobility Particle Sizer (SMPS) right after the exit of the mobility analyzer, before the flow tube (port 0), at four ports along the flow tube (ports 1-4) and at the end of the flow tube (port 5) to obtain the time evolution of the droplet size. During some of the experiments, changes in droplet chemical composition during the evaporation were also monitored using an Aerosol Mass Spectrometer (AMS) (DeCarlo et al., 2006).

5.2 Evaporation model

The measured time evolution of the droplet size was compared to that predicted by an evaporation model (Riipinen et al., 2006). In the model, ammonium sulfate was assumed to be non-volatile, making succinic acid and water the only evaporating compounds. Evaporation of succinic acid was calculated based on its mass flux from a droplet
\[
\frac{dm_{SA}}{dt} = \beta_{SA} \frac{2\pi d_p p M_{SA} D_{SA}}{RT} \ln \left( \frac{1 - \frac{p_{eq,SA}}{p}}{1 - \frac{p_{SA}}{p}} \right),
\]

where the subscript SA refers to succinic acid. Equation 8 is equal to Eq. (3) if the dimension of vapor molecule is not considered for the collision cross-section and diffusional movement of the particle is neglected, both of which are reasonable assumptions when particles are larger than about 20 nm (Nieminen et al., 2010). Equation (8) also takes into account the Stefan flux (the logarithmic term instead of the difference \(p_{SA} - p_{a,SA}\) used in Eq. (3)), although its effect is small when the partial pressure of vapor is much smaller than the total pressure. Evaporation of water was calculated assuming constant instantaneous gas-liquid equilibration of water as succinic acid evaporated.

All evaporated succinic acid was assumed to stay in the same air parcel in which the particles traveled through the flow tube, and, hence, the changes in partial pressure of succinic acid were calculated according to

\[
\frac{dp_{SA}}{dt} = I_{SA} RT \frac{N}{M_i},
\]

where \(N\) is the particle number concentration. The RH inside the flow tube was assumed to be unaffected by the evaporation of water from the droplets. Temperatures of the droplets and the gas were assumed equal, which is justified based on the slow evaporation compared to the time scale of heat transfer.

The Extended Aerosol Inorganics Model (E-AIM; see Sect. 4.2.1) was used with the evaporation model for calculating activity coefficients, droplet water content and density. E-AIM calculates the activity coefficient of organic species independently of inorganic solutes, while for the water activity both organic and inorganic constituents are considered. Overall, the modeling approach was based on simple mixing thermodynamics with ternary mixture properties estimated based on binary aqueous solutions and did not include direct interactions between the organic and inorganic solutes.
5.3 Evaporation of mixed aqueous solution droplets

The TDMA setup was used for studying the evaporation of droplets consisting of succinic acid, ammonium sulfate and water in various initial compositions (Paper V). Comparison of the predicted particle size evolution with the measurements revealed an overestimation of the overall particle size change by the model. When molar fraction of succinic acid was larger than that of ammonium sulfate, the model captured the evaporation well, but when half or more of the solute was ammonium sulfate, the model predicted more evaporation than what was observed. Thus, the overestimation of evaporation seems to be connected to the presence of ammonium sulfate somehow. Interestingly, the measured $F_{org}$ agreed well with the model prediction (Fig. 10).

The results imply that a small amount of ammonium sulfate in the particle does not affect the volatility of succinic acid significantly. In these situations the model captures the evaporation of the mixed aqueous particles well. When ammonium sulfate is the more abundant solute the model overestimates the particle size change compared to the observations. Based on the particle size measurements the results could suggest that ammonium sulfate might enhance the partitioning of succinic acid to particle phase, either by affecting the activity coefficient of succinic acid or through particle phase chemical processes, in case of mainly inorganic particles. However, the chemical composition measurements do not support this conclusion.

The reason for this discrepancy is not known. It is possible that the discrepancy results from several factors including non-volatile impurities detected with the AMS, uncertainty in AMS measurements especially at the end of the evaporation when organic mass is low, and uncertainty in the prediction of water uptake. It was also found that the approach for calculating the building up of evaporating succinic acid in the gas phase overestimates the gas phase saturation with respect to succinic acid. This was not an issue for most of the experiments where mass loadings were low enough to avoid considerable gas phase saturation. Therefore, the uncertainty in the gas phase composition is not likely the reason for overestimation of the evaporation. However, in experiments where AMS was employed the mass loadings were higher and sheath air was not used in the flow tube, which caused considerable uncertainty in the calculation of gas phase composition. For these experiments, ignoring the gas phase saturation with respect to succinic acid was considered a better approach (blue lines in Fig. 10). Overall the results reflect the complicated nature of mixed particles and the difficulty
Figure 10: a) Particle diameter and b) organic molar fraction of the solute ($F_{ordg}$) as a function of time for succinic acid/ammonium sulfate aqueous solution droplets at RH = 80 % (experiment 17 in Paper V). TDMA: geometric mean diameter of log-normal mode fitted to size distribution measured with the TDMA (the errorbars indicate ± one standard deviation of the mode). AMS: $F_{org}$ measured with the AMS (errorbars in y-direction: ± one standard deviation of measured $F_{org}$; errorbars in x-direction are due to estimated longer residence time from flow tube to the AMS compared with the SMPS). Model predictions with gas phase saturation considered (black line) and with assumption of $p_{\infty, SA} = 0$ (blue line) assuming initial dry mass fraction of a non-volatile impurity $X_{mass,dry,ip}$ to be zero. Shaded areas: model prediction with $X_{dry,ip} = 0...20$ %. Modified from figure 3 in Paper V.
in experimental studies of the equilibrium vapor pressures of semi- and low-volatile compounds – the compounds that are of most interest from atmospheric nanoparticle point of view.

The two previous studies on the evaporation of dicarboxylic acids from mixed aqueous solution droplets containing an inorganic salt used sodium chloride as the inorganic salt. Zardini et al. (2010) used the same TDMA method as in Paper V with succinic acid as the organic compound, and found similar overestimation of evaporation rates as in Paper V. Pope et al. (2010b) used single particle methods to study evaporation of droplets where the organic compound was either malonic or glutaric acid, and did not observe an effect of the inorganic salt on the activity coefficients of the organic acids within their experimental accuracy. The modeling approach for the analysis was similar in Pope et al. (2010b) study compared to the TDMA studies (Paper V; Zardini et al., 2010). However, the experimental methods were different: different technique for size determination, time scale, particle size range and organic solutes – all of which could be related to the different results of the effect of inorganic salt.
6 Review of papers and the author’s contribution

This thesis contains five papers. I am solely responsible for the introduction of this thesis.

**Paper I** reports observations of new particle formation events at K-puszta measurement site in Hungary during a 39 days long measurement campaign in May-June 2006. New particle formation was found to be frequent during the campaign: on more than half of the days clear new particle formation with growth of particles towards larger sizes was observed. Only on one day, during which CS was relatively high, there were no signs of new particle formation. The growth rates of sub-20 nm particles increased on average with the particle size, and growth rate values were within typical values observed in the atmosphere. Growth rates were higher during the last half of the campaign when temperature and gas phase concentrations of e.g. monoterpenes and isoprene were also higher. In this paper, I performed most of the data analysis and wrote most of the paper.

In **Paper II** growth rates of 1.5-20 nm particles were analyzed based on 7 years of particle size distribution measurements at SMEAR II measurement station in Hyytiälä, Southern Finland. Growth rates of 3-20 nm particles were found to have similar seasonal variation each year with highest values during summer, while growth rates of sub-3 nm particles were rather constant throughout the year. Especially during summer the growth rates increased with particle size. On average up to 25 % uncertainty was found in growth rate values when size distributions measured with different instruments or different growth rate analysis methods were used. Comparison of the growth rates to meteorological parameters and trace gas concentrations suggested that the concentrations of the volatile organic precursor gases are at least as important of a limiting factor for the particle growth as their oxidation. In this paper, I performed most of the data analysis and wrote most of the paper.

**Paper III** presents a review of current understanding of the organic vapor uptake mechanisms on nanoparticles with particular focus on the particle phase processes, and introduces a conceptual model for salt formation in nanoparticle growth. The relative importance of vapor pressure driven condensation of gas phase oxidation products, salt formation, oligomerization and physical phase of the particle were concluded to depend on particle size. Salt formation was estimated to likely contribute to the growth of < 20 nm particles, while oligomerization may be more important for > 20 nm particles.
I performed the model calculations for this paper and helped in writing the paper.

**Paper IV** introduces nanoparticle growth model MABNAG in which particle phase acid-base chemistry is taken into account using detailed thermodynamics. The model was used for estimating the effect of salt formation on the nanoparticle growth focusing on the boreal forest environment. Salt formation was predicted to be important for the condensation of ammonia and amines but not for organic acids, except at base-rich ambient conditions. It was concluded that salt formation alone is not sufficient to transfer organic acids into compounds with low enough volatility to explain the nanoparticle growth rates observed in the atmosphere, and other particle phase processes or vapors with lower volatility are needed. I built the MABNAG model, performed the model runs, analyzed the data and wrote most of the paper.

**Paper V** reports a laboratory study of evaporation of sub-micron aqueous solution droplets containing succinic acid and ammonium sulfate. Droplet evaporation rates measured with a Tandem Differential Mobility Analyzer connected to a laminar flow tube were slower than predicted with a theoretical model where interactions between the solutes were not accounted for. The model captured the evaporation well when droplets contained more succinic acid compared to ammonium sulfate. When more than half of the solute was ammonium sulfate the model overestimated the decrease in particle size, which could signal that ammonium sulfate lowers the volatility of succinic acid, although chemical composition measurements using Aerosol Mass Spectrometer suggest that the evaporation of succinic acid was still predicted correctly. The reason for the discrepancy was not found, however several uncertainties related to the interpretation of the experiments were identified. In this paper, I performed the model calculations and the related analysis, and wrote most of the paper.
7 Conclusions

In this thesis the growth of atmospheric nanoparticles by uptake of organic vapors was studied based on observations of the variability of the particle growth rates and their relation to ambient conditions. Also modeling approach was used for studying organic uptake processes. Further, properties of organic compounds and their interaction with inorganic particle constituents was studied based on a case study with laboratory experiments. The following can be concluded based on the results:

1) Nanoparticle growth rates in a boreal forest environment in Hyytiälä have a clear seasonal and size dependent variation, which supports the hypothesis of organic condensation controlling the particle growth. Such variations were previously observed for one year of data but here the seasonal pattern was verified based on seven years of measurements. These variations were not caused by uncertainties in the growth rate calculation methods. The seasonal cycle of growth rates of > 3 nm particles and variation with ambient conditions indicate connection between biogenic organic compounds and particle growth. It can be further concluded that particle growth and nucleation are controlled/limited by different compounds and/or processes. This is supported by the distinct diverging seasonal patterns of growth rates of > 3 nm particles and the particle formation rate. Evidence for this is also found from the comparison of growth and formation rates observed at K-puszta to those observed in Hyytiälä: while the growth rates at K-puszta were similar to those observed in Hyytiälä in late spring and early summer, the particle formation rates were higher at K-puszta.

2) Limiting factors and processes related to the particle growth depend on particle size. This is supported by the size dependence in seasonal cycles of particle growth rates and lack thereof for sub-3 nm particle growth rates. The increase in equilibrium vapor pressure with decreasing particle size is likely to limit condensation of organic vapor on sub-3 nm particles in the absence of particle phase processes. This together with the temperature dependence on saturation vapor pressures could explain why sub-3 nm particle growth rates do not increase in the summer with increased organic gas phase concentrations. Particle phase processes that potentially enhance the partitioning of organic compounds on nanoparticles include salt formation and oligomerization, with former likely being more impor-
tant for sub-20 nm size range and the latter possibly playing a significant role for the larger particles.

3) State-of-the-art thermodynamics for particle phase acid-base chemistry predict only a small enhancement of condensation due to salt formation for organic acids at typical conditions for boreal forest, but a significant contribution at high-base conditions. The model predictions using MABNAG thus suggest that processes other than salt formation are needed to explain the existence of short chain organic acids in nanoparticles. On the other hand, further studies of thermodynamic properties of these organic compounds and the applicability of thermodynamics in the smallest nanoparticle size range are needed.

4) The capability of simple mixture thermodynamics to capture the volatility of mixed organic acid/inorganic salt aqueous particles depends on the relative abundance of the solutes. For particles where the main solute was succinic acid, the simplified model representation predicted size change well, suggesting that a small amount of ammonium sulfate does not affect the activity coefficient of succinic acid significantly. When ammonium sulfate was the more abundant solute, the evaporation was overestimated compared to the measured particle size, possibly suggesting interaction between the two solutes, although model prediction agreed with the measured chemical composition of the particles. The interpretation of such evaporation experiments was found to be associated with uncertainties which demonstrates the difficulty in determining evaporative properties of compounds that have low saturation vapor pressures. In the future it is important to develop experimental techniques for determining the thermodynamic properties of atmospherically relevant organic compounds that have low saturation vapor pressures.

The increased number of both atmospheric and laboratory studies and the developments in instrumentation have increased our understanding of the growth of atmospheric nanoparticles and the ability to represent it in climate models. This thesis has contributed to this progress by quantifying the variability of nanoparticle growth rates and by presenting their relation to ambient conditions, as well as by evaluating the performance of current thermodynamic modeling in capturing behavior of simplified laboratory aerosol and ambient nanoparticles. Several unknowns are still associated with the atmospheric nanoparticle growth. In the future, both field and laboratory studies tracking simultaneously gas and particle phase composition are highly desired.
On one hand, laboratory studies with simplified chemical systems are of great value in determining the missing thermodynamic properties, and on the other hand, laboratory experiments simulating the complex nature of atmospheric aerosol particles are needed as the importance of the processes and the properties of aerosol are likely to be composition dependent.
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