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## INSIGHTS INTO ATMOSPHERIC NUCLEATION

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Academic dissertation

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## **Insights into atmospheric nucleation**

Mikko Juhani Sipilä

University of Helsinki, 2010

### **Abstract**

Atmospheric aerosol particles have a strong impact on the global climate. A deep understanding of the physical and chemical processes affecting the atmospheric aerosol – climate system is crucial in order to describe those processes properly in global climate models. Besides the climatic effects, aerosol particles can deteriorate e.g. visibility and human health.

Nucleation is a fundamental step in atmospheric new particle formation. However, details of the atmospheric nucleation mechanisms have remained unresolved. The main reason for that has been the non-existence of instruments capable of measuring neutral newly formed particles in the size range below 3 nm in diameter. This thesis aims to extend the detectable particle size range towards close-to-molecular sizes (~1nm) of freshly nucleated clusters, and by direct measurement obtain the concentrations of sub-3 nm particles in atmospheric environment and in well defined laboratory conditions.

In the work presented in this thesis, new methods and instruments for the sub-3 nm particle detection were developed and tested. The selected approach comprises four different condensation based techniques and one electrical detection scheme. All of them are capable to detect particles with diameters well below 3 nm, some even down to ~1 nm. The developed techniques and instruments were deployed in the field measurements as well as in laboratory nucleation experiments. Ambient air studies showed that in a boreal forest environment a persistent population of 1-2 nm particles or clusters exists. The observation was done using 4 different instruments showing a consistent capability for the direct measurement of the atmospheric nucleation.

The results from the laboratory experiments showed that sulphuric acid is a key species in the atmospheric nucleation. The mismatch between the earlier laboratory data and ambient observations on the dependency of nucleation rate on sulphuric acid concentration was explained. The reason was shown to be associated in the inefficient growth of the nucleated clusters and in the insufficient detection efficiency of particle counters used in the previous experiments. Even though the exact molecular steps of nucleation still remain an open question, the instrumental techniques developed in this work as well as their application in laboratory and ambient studies opened a new view into atmospheric nucleation and prepared the way for investigating the nucleation processes with more suitable tools.

Keywords: Atmospheric aerosols, atmospheric clusters, nucleation, aerosol particle detection

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## List of publications

This thesis consists of an introductory review, followed by five research articles reproduced with the permission of the journals concerned. In the introductory part of this thesis, these papers are cited according to their following roman numerals.

**I** Mordas, G., Sipilä, M., and Kulmala, M., Nanometer particle detection by the condensation particle counter UF-02 proto, *Aerosol Sci. Technol.* 42:521-527, 2008. Copyright 2008. Mount Laurel, NJ. Reprinted with permission.

**II** Kulmala, M., Riipinen, I., Sipilä, M., Manninen, H., Petäjä, T., Junninen H., Dal Maso, M., Mordas, G., Mirme, A., Vana, M., Hirsikko, A., Laakso, L., Harrison, R. M., Hanson, I., Leung, C., Lehtinen, K. E. J., and Kerminen, V.-M., Toward direct measurement of atmospheric nucleation, *Science*, 318, 89-92, 2007. Reprinted with permission.

**III** Sipilä, M., Lehtipalo, K., Kulmala, M., Petäjä, T., Junninen, H., Aalto, P. P., Manninen, H. E., Vartiainen, E., Riipinen, I., Kyrö, E.-M., Curtius, J., Kürten, A., Borrmann, S., and O'Dowd C.D., Applicability of condensation particle counters to detect atmospheric clusters, *Atmos. Chem. Phys.* 8:4049-4060, 2008. Reprinted under the Creative Commons License.

**IV** Sipilä, M., Lehtipalo, K., Attoui, M., Neitola, K., Petäjä, T., Aalto, P. P., O'Dowd, C. D., and Kulmala, M., Laboratory verification of PH-CPC's ability to monitor atmospheric sub-3nm clusters, *Aerosol Sci. Technol.*, 43, 126-135, 2009. Copyright 2009. Mount Laurel, NJ. Reprinted with permission.

**V** Sipilä, M., Berndt, T., Petäjä, T., Brus, D., Vanhanen, J., Stratmann, F., Patokoski, J., Mauldin III, R. L., Hyvärinen, A.-P., Lihavainen H., and Kulmala, M., The role of sulphuric acid in atmospheric nucleation, *Science*, 327, 1243-1246, 2010. Reprinted with permission.

# 1 Introduction

Climate change is one of the largest threats that mankind has ever faced. Predicting the future climate from local to global scales requires a deep scientific understanding of all numerous factors and feedback mechanisms affecting the Earth's climate system; however, large gaps in our knowledge still exist. These gaps include serious, possibly even fatal, feedback mechanisms and consequences, such as how vast amounts of methane, deposited as hydrates in permafrost regions and in marine sediments, will be released with warming temperatures (Lelieveld, 2006), what is the fate of rainforest ecosystems (Malhi et al., 2008), or how the oceans' circulation will change with changing climate (Hansen et al., 2004). One great danger associated with these feedback mechanisms is that certain large-scale Earth systems can irreversibly transform or collapse if forced across some critical threshold (Hansen et al., 2007; Parks, 2009). Indisputable evidence of such a "tipping-point" behaviour is the rapid loss of Arctic sea-ice (Serreze et al, 2007) where the probability to recover is considered to be very low (Parks, 2009).

Ignorance of different feedback mechanisms add to the uncertainty of future climate predictions, but even the estimates of the present climate forcing due to anthropogenic activities include poorly understood factors. According to the Intergovernmental Panel on Climate Change (IPCC), the largest uncertainty in current climate forcing estimates is the effect of aerosols (IPCC, 2007). The effect of human alteration of the atmospheric aerosol system is estimated to have a negative radiative forcing (cooling effect on climate) but with a large uncertainty range from  $-0.4$  to  $-2.7 \text{ W m}^{-2}$  (in 2005). If compared to the radiative forcing estimate for long lived greenhouse gases (carbon dioxide, methane, nitrous oxide and halocarbons) of  $+2.64 \text{ W m}^{-2}$  (in 2005) the cooling effect of aerosols ranges between negligible and complete counteraction for the effect of greenhouse gases at their present level.

Each cubic centimetre of air consists of approximately  $2.5 \cdot 10^{19}$  gas molecules. In any environment, the air also carries from tens (Koponen et al., 2003) up to hundreds of thousands (Mönkkönen et al. 2005) liquid or solid aerosol particles per cubic centimetre. The term aerosol is defined as the combination of these particles and the gas (usually air) they are floating in. The size of the atmospheric particles ranges from molecular clusters with a diameter of about 1 nm to dust particles and cloud droplets with diameters of tens or even hundreds of micrometers. Aerosol particles can either be emitted into the atmosphere as primary particles or formed from atmospheric vapours by gas-to-particle conversion. Those particles are called

secondary aerosol particles. Primary particles are, for example, spores, pollen and airborne bacteria and viruses, soot and smoke, sea salt particles and dust (Pöschl, 2005). Depending upon particle size, chemical nature and concentration they can have negative health effects (Pöschl, 2005, and references therein). While the effect of aerosols on health is important, the motivation for the present study arises from their effect on climate.

Aerosol particles can impact the Earth's radiation budget (and therefore also climate) by scattering and absorbing solar radiation. These combined processes are called the direct effect, which radiative forcing is currently estimated to be between  $-0.1$  and  $-0.9 \text{ W m}^{-2}$  (IPCC, 2007). Recent observations suggest a slightly smaller range of  $(-0.3 \pm 0.2) \text{ W m}^{-2}$  (Myhre, 2009). Aerosol particles also act as seeds for cloud droplets; this is called indirect effect. Every cloud droplet is formed by water condensation on an aerosol particle. The ability of an aerosol particle to act as such a cloud condensation nucleus (CCN) depends upon the particle size, chemical properties and the super-saturation of the condensing water vapour (Pruppacher and Klett, 1997). The concentration of CCN affects both the concentration and size of the cloud droplets and thus, in turn, the optical properties (Twomey effect, or the first indirect effect; Twomey, 1974) and lifetime (Albrecht effect, or the second indirect effect) of the cloud as well as precipitation (Rosenfeld et al., 2000; Ramanathan et al., 2001; Rosenfeld et al., 2008). The IPCC radiative forcing estimate for the first indirect aerosol effect ranges from  $-0.3$  to  $-1.8 \text{ W m}^{-2}$  forming the largest single source of uncertainty in understanding the climate change (IPCC, 2007). The level of understanding of the second indirect effect is so poor (see e.g. Penner et al., 2006) that no estimate for that is given. Understanding the physical and chemical processes affecting the Earth's aerosol system is necessary to properly include aerosols in global climate models.

Nucleation is the initial step of new particle formation from precursor vapours (Seinfeld and Pandis, 2006; Kulmala, 2003). During homogeneous nucleation, small clusters are formed from the supersaturated vapour(s) in the gas phase via collisions of those vapour molecules. Nucleation can occur also on the surface of an existing particle. This process is called heterogeneous nucleation. The energy barrier for cluster formation in heterogeneous nucleation is typically lower than that for homogeneous nucleation (see e.g. Kulmala et al., 2007a; Winkler et al., 2008a), and in the presence of any surface, heterogeneous nucleation is usually favoured. Ion-induced nucleation is a special form of heterogeneous nucleation. In this case, the phase transition occurs on a molecular ion cluster. Nucleation can involve only a single gas phase species, in which case it is called homomolecular nucleation, or two (binary nucleation), three (ternary nucleation) or even more precursor species.



Nucleation occurs frequently in the atmosphere (Kulmala et al., 2004). Figure 1 shows a typical example of such a nucleation event measured at SMEAR II station (Hari and Kulmala, 2005) in Hyytiälä, Southern Finland (see also Mäkelä et al., 1997). Here, it can be seen that the continuous population of so called Aitken-mode (see e.g. Hinds, 1999) particles in the size range from some tens to roughly a hundred of nanometers is diluted in the morning due to boundary layer mixing. Then, slightly before noon, newly formed particles appear at smallest size channel (3 nm) of the detector. After formation, these particles grow in time contributing to the background Aitken-mode population again next day. This type of day time nucleation event occurs in Hyytiälä approximately 60 to 120 times per year (Kulmala et al., 2010) with the frequency peaking in spring and autumn.

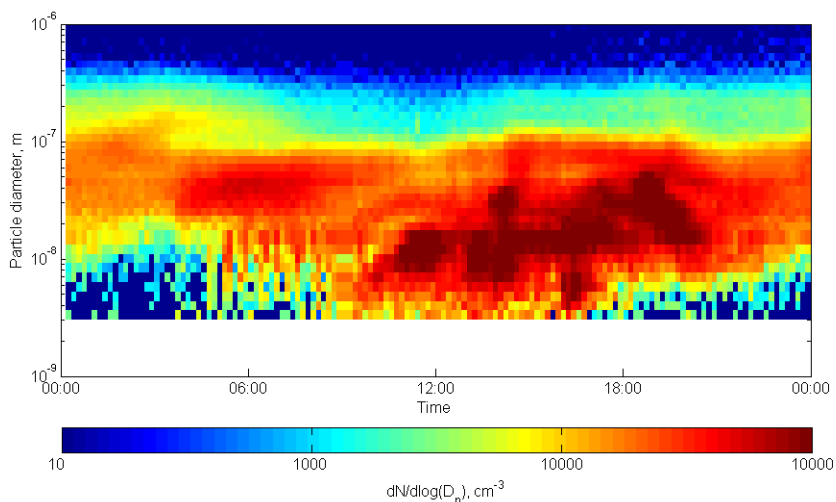


Figure 1. 24 hour surface plot showing the development of the particle size distribution during a nucleation event day. This data was obtained with an ordinary DMPS system. Thus no information on sub-3nm concentrations can be obtained.

Even though new particle formation is a global phenomenon (Kulmala et al., 2004), atmospheric nucleation mechanisms are still not understood in detail and several pathways have been proposed (Kulmala, 2003). Atmospheric observations have shown that nucleation is often strongly connected on the abundance of gas phase sulphuric acid (Weber et al., 1996; Birmili et al., 2003; Sihto et al., 2006; Riipinen et al., 2007; Kuang et al., 2008; Paasonen et al., 2010). Sulphuric acid concentrations associated to nucleation in the atmosphere are typically in the range

of  $10^5$  to slightly less than  $10^8$  molecules  $\text{cm}^{-3}$ . The saturation vapour concentration of sulphuric acid is of the order of  $10^{11}$  molecules  $\text{cm}^{-3}$  (see Vehkamäki et al., 2002) and therefore other compounds are required to assist the nucleation. Some potential mechanisms which have been suggested and studied include binary nucleation of sulphuric acid and water (e.g. Mirabel and Katz, 1974; Jaecker-Voirol and Mirabel, 1989; Vehkamäki et al., 2002), ternary nucleation with ammonia as a third body (e.g. Korhonen et al., 1999; Napari et al., 2002), nucleation of sulphuric acid together with certain organic oxidation products (Bonn et al., 2008; Metzger et al., 2010), ion induced or ion mediated nucleation (Turco et al., 1998; Yu and Turco, 2001; Laakso et al., 2002, Kazil et al., 2008; Yu, 2010), kinetic (barrierless) nucleation – a special form of homogeneous nucleation (McMurry, 1980; Lushnikov and Kulmala, 1995; Clement and Ford, 1999), and activation nucleation – i. e. heterogeneous nucleation on pre-existing clusters (Kulmala et al., 2000; 2006). Nevertheless, the exact mechanisms of nucleation remain an open question. This thesis attempts, by means of direct measurements of freshly nucleated clusters in an ambient environment and laboratory experiments, to shed light on the mystery of atmospheric nucleation.

Once formed, freshly nucleated clusters can grow by condensation of supersaturated vapours. These vapours can be partly the same as those that are involved in the nucleation process. However, due to decreasing Kelvin effect (Seinfeld and Pandis, 2006) with increasing particle size, it is also plausible that several other species, such as ammonia (Smith et al., 2005) or organics (O'Dowd et al., 2002a; Smith et al., 2008), can condense on particles. Condensational growth of ultrafine particles is a relatively slow process. Depending upon the environment, the growth rates are typically few nanometres per hour (Kulmala et al., 2004). In certain coastal areas (O'Dowd et al., 2002b), polluted megacities (Iida et al., 2008), and some other environments, the growth rate can exceed 20 nm/h. Particles can grow also by colliding and sticking with each other – this process is called coagulation. Coagulation with larger pre-existing particles is also the main sink for newly formed nanoparticles (Kerminen et al., 2001). After reaching a diameter of 50 – 100 nm, which typically takes from hours to tens of hours, particles can act as CCN and affect the climate via impacting cloud properties (Kerminen et al., 2005).

Motivation for this work emerged from the threat of climate change. As the atmospheric aerosol system is strongly coupled to climate, the main objective of this thesis is to gain insight into atmospheric nucleation mechanisms. To achieve this goal, the following specific objectives were set:

- 1) To establish scientific methods for the detection of sub-3 nm particles and clusters.
- 2) To perform the first direct measurements of the concentrations and variability of sub-3nm neutral particles in the atmosphere.
- 3) To explain the discrepancy between laboratory experiments and ambient observations on the role of sulphuric acid in atmospheric nucleation.

The first of the specific objectives was approached by testing and modifying the existing techniques, and developing new detection methods and instrumentation for the direct measurement of the freshly formed nano-sized clusters (**Papers I, II, III, IV and V**). As can be seen from Figure 1, no information on sub-3 nm particles can be obtained using existing commercial measurement techniques. Thus, a major aim was to extend the detectable particle size range from the 3 nm limit of commercial instruments down to 1-2 nm sizes. The intent was to test the applicability of several techniques to find the most suitable methods for nano-cluster detection.

The second sub-objective was approached by applying these new techniques and instruments for field measurements at a regional background station (SMEAR II) in Southern Finland. Here, the intent was to directly observe atmospheric nucleation in-situ and to gain knowledge on the existence and dynamics of sub-3 nm particles and clusters (**Papers II and III**).

Finally, to address the third sub-objective, the developed instrumental techniques were utilized in laboratory nucleation experiments under well defined conditions to gain insight into the very first steps of the nucleation process which have thus far been beyond the detection limits of commercially available instruments (**Paper V**).

The organization of this thesis is based on the three above mentioned sub-objectives. While the main objective of this work is atmospheric nucleation, especially the results related to development of the nano-particle detection methods form a separate solid ensemble with the range of their applications crossing the borders of atmospheric sciences.

## **2 Development of particle detectors**

This section comprises an introduction into calibration procedures (chapter 2.1), descriptions of condensation based techniques developed and/or tested in the

present work (chapter 2.2), as well as a presentation of a detector based upon artificial charging and electrical detection (chapter 2.3). Before proceeding, a few words about the terminology used are required.

In the following sections, sub-3 nm particles will often be called either clusters or nano condensation nuclei (nano-CN, Zhao et al., 2010). A cluster, by definition, consists of two or more molecules without a chemical binding. The instruments, which are based upon measurement of mobility, or diameter, do not yield the information whether the detected nano-particle is a particle or cluster at all, or a large molecule. Thus Zhao et al. (2010) suggested the use of term ‘nano-CN’ rather than ‘cluster’, unless the exact chemical nature is known. However, the terminology suggested by Zhao et al. (2010) cannot be applied in case of instrumentation based upon detection methods other than involving condensation (for condensation based techniques, see chapter 2.2), for example, electrical detection methods (chapter 2.3). Therefore, because no consensus about the terminology yet exists, the words ‘sub-3 nm particle’, ‘cluster’ and ‘nano-CN’ can be taken as synonyms throughout this summary part of this thesis.

Another important point to stress is the definition of diameter. The diameters yielded by different instruments presented in this work are based on calibrations (e.g. PHA-UCPC described in chapter 2.2.2), or the direct measurement of particle mobility distribution (NAIS, chapter 2.3). Classification of calibration aerosol is based upon the different mobilities of particles (chapter 2.1). Thus, at the end, the particle diameter obtained using any of these instruments is mobility diameter (e.g. Hinds, 1999). For spherical particles the difference between the mobility diameter and geometrical diameter is approximately the average diameter of the colliding gas molecules (air in atmosphere) (Tammet, 1995). Thus, for spherical particles, the mobility diameter is ca. 0.3 nm larger than geometric diameter (Tammet et al., 1995; Mäkelä et al., 1996; Ku and Fernandez de la Mora, 2009). For particles possessing a more complex shape the diameter is not well defined. Throughout this thesis, the reported diameters are mobility diameters, unless otherwise explicitly expressed.

## **2.1 Generation of calibration aerosol**

Calibration experiments are necessary for any kind of detector development. Thus this section begins with a short introduction into calibration and testing procedures. Calibration of aerosol detectors – condensation particle counters (CPC) in this work

– in the sub-3nm range is challenging. This difficulty arises mostly because the production of monodisperse calibration aerosol in that size range requires novel methods not yet used on a regular basis within the community of aerosol scientist. Also, the necessary instrumentation and knowledge about the practices is not abundant. Fortunately, in recent years, much effort has been placed upon developing methods to generate and classify particles with high resolution in the nanometre size range. Key scientists in this development have been J. Fernández de la Mora and his co-workers (e.g. Fernández de la Mora et al., 1998; Rosser and Fernández de la Mora, 2005; Ude and Fernández de la Mora, 2005, Fernández de la Mora and Attoui, 2007).

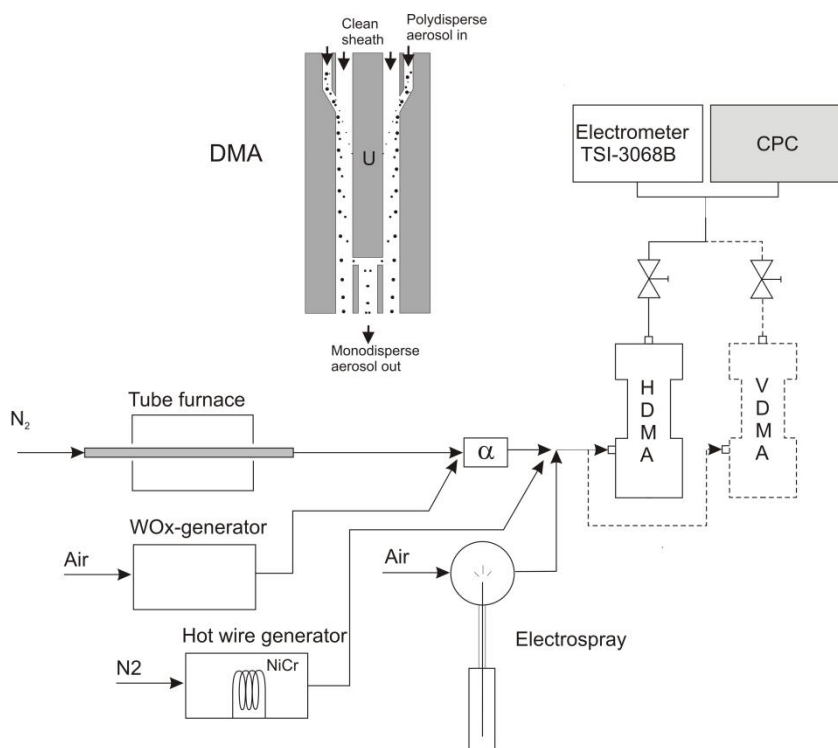


Figure 2. Experimental setup used in the calibration experiments. HDMA refers to a high mobility resolution Herrmann differential mobility analyzer (DMA) and VDMA to a Vienna type DMA (see text for more details). Depending upon the aerosol generator used, particles need to be charged in a radioactive charger (in this work Am-241  $\alpha$ -source) before they can be classified according to their electrical mobility in the DMA. As a reference instrument an electrometer is used. Schematic representation of the operation of a DMA is also shown.

Several methods to produce calibration aerosol exist. The methods used in this study include evaporation – nucleation technique (Scheibel and Porstendörfer, 1983) in which material, usually metals or NaCl, is evaporated in a heated furnace. A carrier flow containing the evaporated vapour is then cooled down resulting in super-saturation and nucleation of the precursor species. The produced aerosol sample then needs to be charged for subsequent classification. Charging can be accomplished, for example, by means of a bipolar diffusion charger (see e.g. Wiedensohler and Fissan, 1991, and references therein) that often applies radioactive decay for ion production, or by a unipolar diffusion charger where ions are produced by a corona discharge. Ions produced by either charger can also be used as test particles in the ~0.9-1.5 nm size range (see e.g. Asmi et al., 2009) if the knowledge about their chemical composition is not required.

Evaporation of the material can also be accomplished by directly heating the wire made of wanted metal with electric current (Peineke et al., 2006). The advantage of this hot-wire method is that depending upon the material it can produce high concentrations of singly charged particles in the nanometre size range (Attoui and Fernández de la Mora, 2007). In this work, different evaporation – nucleation techniques were used to generate calibration aerosol from silver and ammonium sulphate (tube furnace), chrome – nickel (hotwire-generator), and tungsten oxides (Grimm model 7.860 WO<sub>x</sub>-generator). It should be noted, that the particle chemical composition in case of furnace generated particles can differ from the bulk material in case of ammonium sulphate that dissociates in the furnace temperatures.

Another important method applied in the present work is the electrospray-technique (Smith, 2000). In this method, a minute quantity of precursor substance (preferably some salt) is dissolved in a solvent (usually water or alcohol). This solution is then pushed through a capillary needle extending into a grounded electrospray chamber through which a carrier air streams. A high voltage (some thousands of volts) is applied to the solution container and thus a strong electric field affects the solution in the tip of the capillary needle (the solution needs to be electrically conductive). The electric field rips the solution into small (~micrometers) strongly charged droplets, which immediately start to evaporate in the carrier flow. While evaporating the charge density in the droplets increases. Finally, repulsive Coulombic forces overcome the surface tension of the droplet and the droplet explodes yielding a spectrum of molecular ion clusters of the precursor species. Ude and Fernández de la Mora (2005) determined the mobilities and masses for a series of electrosprayed tetra-alkyl-ammonium halide salts. These mobility standards are extremely useful in calibrating high flow DMAs, as well as CPCs.

Particles of the required size need to be separated from the generated particle (or ion) spectrum. This separation is accomplished by means of a differential mobility analyzer (DMA; Knutson and Whitby, 1975) in which the aerosol sample travels between two coaxial cylinders (electrodes). Initially, the sample is isolated from the wall of the inner cylinder with a particle free sheath flow. An electric field is applied between the cylinders causing the charged particles drift cross the sheath flow. Particles with certain electrical mobility experience a trajectory inside the DMA such that they hit a thin exit slit in the inner electrode and proceed to the detectors (Figure 2). For non-diffusing particles (large particles), the resolution of the DMA is defined as a ratio between the sample flow and the sheath flow. For smaller particles, diffusion broadening (Stolzenburg, 1988) significantly deteriorates the resolution. In field measurements, a CPC is usually used as a detector after DMA. In calibration experiments, an electrometer is used as a reference instrument in parallel with the CPC (Liu and Pui, 1974).

Since this work focuses in the particle size range below the 3 nm detection limit of commercial instruments, the requirements for the DMA are different than for those used for separating larger particles e.g. in particle size distribution measurements. For the purposes of this work, a high resolution (2-5% FWHM in mobility space at  $Z=1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  –  $\sim 1.5 \text{ nm}$  in mobility diameter) DMA is required (Fernández de la Mora et al., 1998; Rosser and Fernández de la Mora, 2005; Steiner et al., 2010). In **Paper I**, such a DMA was not available, and thus the calibrations were performed with an ordinary short Vienna-type DMA (Winklmayr et al., 1991) where the resolving power (Reischl et al., 1997) is far from that of high resolution instruments. In all other instrument calibrations a high resolution Herrmann-DMA (Herrmann et al., 2000) was used. High resolution is achieved by using extremely high sheath flow velocities, in some cases exceeding 1 Mach (Attoui, 2009). These high sheath gas velocities allow one to use high separation voltages and minimize the diffusion broadening of the DMA transfer function. Such high flow speeds result in very high Reynolds numbers up to 35 000 (Herrmann et al., 2000). This type of flow would normally be turbulent. To alleviate this effect, in those DMAs, large laminarization sheets combined with a conical section to smoothly accelerate the flow are used prior the classification section. With this special design, flows stay laminar through the classification section of the DMA. The disadvantage of these high resolution DMAs is that they are not applicable in field measurements owing to very small area of the transfer function. Because of the narrow transfer function the particle concentrations at the DMA output are very low and counting statistics becomes poor.

The calibration setup used in the experiments included in this study is depicted in Figure 2. Though several aerosol or ion generators are shown in the same figure, usually only one is used at time. In some experiments, described in **Papers I** and **IV**, two generators and/or two DMAs were used in parallel.

## 2.2 Condensation particle counters (CPC)

Nanometre-sized small particles in supersaturated high vapour pressure vapour can rapidly grow by condensation to micrometer-sizes, where they can be optically detected. Condensation Particle Counters (CPC), traditionally called condensation nucleus counters (CNC), are based on this feature. Operation of a CPC is comprised of the following steps: i) Creation of mixture of aerosol sample and supersaturated vapour (typically alcohol or water, often referred as "working fluid"), ii) growth of the aerosol particles by condensation of the working fluid, and iii) optical detection and counting of the droplets.

The performance of a CPC is often described by the 50% detection limit (D50) which is defined as a diameter of the smallest particles of which 50% are successfully counted. Modern commercially available CPCs have D50 of 3 nm or larger. Because nucleation in the atmosphere occur close to molecular sizes (~1 nm), those CPCs cannot detect particles immediately after nucleation, but the particles need to grow into the detection regime of the CPC. Therefore, with a common CPC, only indirect information of the nucleation process can be obtained. One of the main aims of this work was to develop methods to extend the measurable particle size range from 3 nm to closer to the size of freshly nucleated clusters.

Several methods to generate the supersaturation exists (e.g. McMurry et al., 2000). In CPC technology, the most commonly used is **i)** a conductive cooling type laminar flow design (Agarwal and Sem, 1980) in which the air flow is saturated with the working fluid in a heated saturator, and directed to a cooled condenser where the vapour supersaturates due to cooling of the flow. The aerosol sample is either laminarly mixed with the saturated air flow prior the condenser (Stolzenburg and McMurry, 1991), or the sample flow itself travels through the saturator (Agarwal and Sem, 1980). Such a laminar flow design works for most condensing vapours. For vapours diffusing faster than heat (e.g. water), the supersaturation needs to be created by **ii)** vapour diffusion from the warm wetted walls of the condenser to the cooled aerosol sample flow (Hering and Stolzenburg, 2005). Another method to



produce the supersaturation is **iii**) turbulent mixing (e.g. Kousaka et al., 1982; Okuyama et al. 1984; Sgro and Fernandez de la Mora, 2004). In a mixing type CPC, the saturated warm air is turbulently mixed with a cooled aerosol sample flow. Historically, the first method to produce supersaturation was **iv**) an adiabatic expansion of a vapour – aerosol mixture (Aitken, 1888; Wilson, 1897; Wagner, 1985; Kürten et al., 2005; Winkler et al., 2008a;b). Since one of the main objectives of this work was to develop methods for extending the detectable particle size range to smaller particles, all of the above mentioned methods, with the exception of the water based laminar flow design, were studied and used in this work. The conductive cooling type laminar flow CPCs were used in all studies described in **Papers I-V**, the expansion type CPC in **Paper III**, and the mixing type CPC in **Paper V**.

The main problem associated in the application of the CPC technique for detection of particles with diameters approaching the molecular scale of ~1 nm is connected to the Kelvin effect (Seinfeld and Pandis, 2006). The Kelvin effect relates the surface curvature of a small particle to saturation vapour pressure on the surface. The smaller the particle is, the higher the required vapour pressure is to keep the particle surface in equilibrium. The diameter required for equilibrium in a given saturation ratio is called the critical diameter, or Kelvin diameter. If the vapour pressure of a certain vapour is smaller than the saturation vapour pressure on the particle surface the vapour evaporates from the particle. If the vapour pressure is higher, the vapour condenses on the particle. Figure 3a shows an example of the critical particle diameter  $d^*$  as a function of saturation ratio  $S$ . Here, *n*-butanol is chosen as an example vapour since *n*-butanol is the most commonly used working fluid in CPCs. This approach is only valid for particles composed of pure liquid of the same substance as the vapour. However, it can be used here as a first approximation. Figure 3a clearly shows that with particle diameter approaching the sub-3 nm range the saturation ratio needed to initiate condensational growth increases rapidly. Technically, it is not challenging to increase the saturation ratio inside a CPC. All that need to be done is to increase the temperature difference between the saturator and condenser. However, with high saturation ratio the working fluid starts to nucleate homogeneously producing artificial droplets that are then counted the same way as the droplets formed on the seed particle. The homogeneous nucleation rate as a function of  $S$  at temperature of 283.15K calculated from classical nucleation theory (see e.g. Viisanen and Strey, 1994) is depicted in Figure 3b. From Figures 3a&b it can be immediately seen that decreasing the detectable particle size below some 3 nm in diameter by means of increasing the supersaturation is limited by droplet formation via homogeneous nucleation.

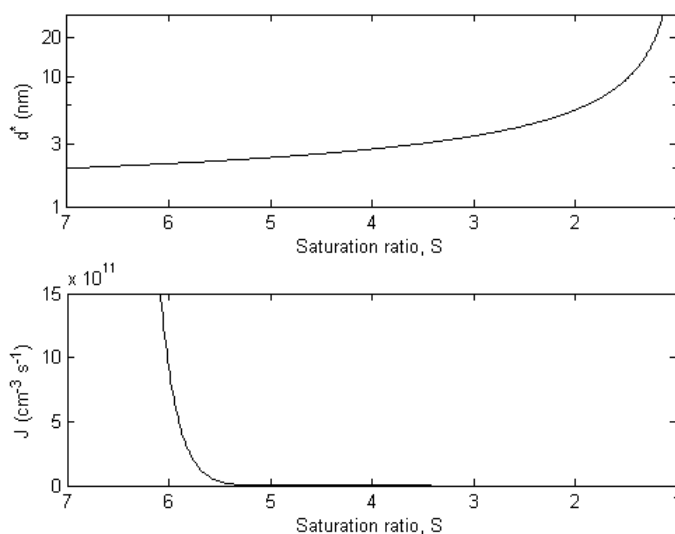


Figure 3. Critical particle diameter (Kelvin diameter) as a function of saturation ratio of *n*-butanol (a) and homogeneous nucleation rate calculated from classical nucleation theory (b) at a temperature of 283.15 K.

The above consideration is based on the Kelvin effect and homomolecular condensation and is not exact. In reality, heterogeneous nucleation is often favoured over homogeneous nucleation and condensation, meaning that seed particles smaller than the critical diameter  $d^*$  can be activated for condensational growth. This effect is examined extensively for example by Winkler et al. (2008a). Winkler et al. (2008b) concluded that for example in propanol vapour, particles down to diameter of 1.4 nm are activated prior the onset of homogeneous nucleation. The activation probability (i.e. fraction of seed particles that are activated for growth) depends notably on the particle diameter, but also on the charge carried by the particle (Winkler et al., 2008a; Sipilä et al., 2008), the sign of the charge (Winkler et al. 2008a), particle chemical composition (O'Dowd et al., 2002a; 2004; Kulmala et al., 2007a) as well as on the concentration of seed particles (**Paper IV**). Concerning activation, an important chemical property is the particle solubility (to the working fluid) because a soluble seed particle can take the initial steps of growth by absorbing the working fluid. The theory describing this effect is called nano-Köhler theory (Kulmala et al., 2004), which is analogous to the Köhler theory that describes the cloud droplet formation on water soluble CCN (Pruppacher and Klett, 1997). **Papers III** and **IV** show, in line with Winkler et al. (2008b), that particle activation down to almost arbitrarily small seed particle sizes (mobility diameter of smallest test particles used in **Paper IV** was  $\sim 1.1$  nm) takes place before

homogeneous nucleation start to occur. In these papers, a method to distinguish between the butanol droplets formed on a seed particle and the droplets resulting from homogeneous nucleation is introduced.

Butanol and water are most commonly used as working fluids in CPCs. The main requirements for the working fluid are non-toxicity and a high saturation vapour pressure to grow particles to optically detectable sizes. Since CPCs are used usually at ambient conditions in presence of water vapour, the water solubility of the working fluid might also become an issue, because the dissolved water can deteriorate the saturation vapour pressure of working fluid. Due to these reasons, commercial CPCs usually work either with n-butanol or water. However, from the point of view of seed particle activation and homogeneous nucleation behaviour the working fluid has a strong impact. This impact was studied by Iida et al. (2009), who went through hundreds of organic compounds to find a working fluid that can activate the smallest particles possible in absence of homogeneous nucleation. Their work formed the basis for the particle size magnifier used in **Paper V**. This technique will be discussed further in section 2.2.4.

Besides the occurrence of homogeneous nucleation, the loss of sampled nanoparticles by diffusion also limits the performance of CPCs in the nucleation mode size range (below few tens of nanometers). Diffusion losses can be minimized using as short flow lines and as high aerosol sample flows as possible. However, care should be taken that the flow stays laminar as turbulence in the flow tends to increase the diffusion losses. The main motivation for the development of the particle size magnifier, described in section 2.2.3 and **Paper V**, was that such a design allows one to use high sample flows until the starting point of condensation, thereby minimizing the diffusion losses.

In the following sections, the condensation particle counters used in this work are presented in the chronological order. The emphasis here is the application of pulse height analysis for the ultrafine condensation particle counter (PHA-UCPC, section 2.2.2) for nano-CN detection, and the particle size magnifier (PSM, section 2.2.4) developed and constructed during this work. This focus is because in the development of those two above mentioned techniques, the author's contribution has been largest. Table 1 provides a "historical" view to the development of CPC techniques presented in this work. In the table, the 50% detection limit (D50) is given and stability and reproducibility is estimated.

Table 1. Different condensation particle counters used in this work, time span of the use, 50% detection limit (D50), and stability and reliability of the instrument. Even though with PHA-UCPC a 50% detection limit not better than slightly below 3 nm can be achieved, the PHA method allowing for the detection efficiency correction extends the measurable particle size range down to ~1.5 nm. Thus, the PHA-UCPC performance is fully comparable with the PSM.

CPC	Time span used	D50 (nm)	stability/reproducibility
UF-02proto	2006	1.8 <sup>*</sup>	Poor <sup>***</sup>
PHA-UCPC	2007 - >	2.7 <sup>**</sup>	Excellent
E-CPC	2007	~2	Fair
PSM	2009 - >	1.8	Excellent

\*No high resolution DMA used in calibration.

\*\*with the PHA-UCPC, the detection efficiency can be accounted for, yielding to unity detection efficiency down to ca. 1.5 nm. Thus the D50 sizes cannot be directly compared.

\*\*\* refers to the situation where supersaturation is increased so much that 1.8 nm D50 size is achieved. With nominal settings, the stability is much better.

## 2.2.1 UF-02proto CPC

The butanol based condensation particle counter UF-02proto was developed by Mordas et al. (2005). The design is, to some extent, similar to the UM-UFCNC (prototype of TSI-3025 CPC) presented by Stolzenburg and McMurry (1991). For example the transportation of the aerosol sample efficiently to the condenser follows the design of UM-UFCNC. The special feature of the UF-02proto CPC is a swirling flow inside the condenser. According to Mordas et al., (2005), this flow design minimizes nano-particle losses and enlarges the supersaturated region thereby increasing the detection probability.

Using nominal operation settings, the lowest detection limit of the UF-02proto CPC lays at 4.4 nm (Mordas et al., 2005). In the study presented in **Paper I**, it was recognized that much higher levels of super-saturation can be applied before homogeneous nucleation starts to interfere with the measurement. Super-saturation was increased by simply varying the temperatures of the saturator and the condenser. A D50 size of  $(1.8 \pm 0.2)$  nm was achieved with a level of background signal from homogeneous nucleation corresponding to approximately 10 activated particles  $\text{cm}^{-3}$ . The reason for this superior performance is assumed to be related to the geometrical design of the instrument. Stability of the tuned UF-02proto CPC was unfortunately poor. The reason for that was associated to occasional condensation of butanol vapour in the optical detector and in the lines after the detector deteriorating the droplet counting and flows inside the CPC. Thus, after

such an occasion the CPC needed to be dried. The UF-02proto CPCs were used in a field study presented in **Paper II**.

### **2.2.2 Pulse height analysing ultrafine condensation particle counter (PHA-UCPC)**

As already discussed above, the co-occurrence of homogeneous nucleation of the working fluid interferes with the particle measurement if a high super-saturation is used. Pulse height analysis (PHA) of white light scattered by the (butanol) droplets formed in the condenser of a laminar flow CPC offers a method to overcome this problem. The operational principle of a PHA-UCPC is based on the axial gradient of butanol super-saturation inside the condenser (Stolzenburg, 1988; Ahn and Liu, 1990) (Fig. 4). The particle activation probability is dependent on the super-saturation (see Fig. 3). The smaller the particle the further it must travel inside the condenser before it is activated for growth. Particles larger than ~ 10 nm practically become activated immediately after entering the condenser and grow throughout their passage inside the condenser therefore reaching a relatively large final droplet size. Smaller particles, which are activated closer to the super-saturation maximum, have less time for condensational growth and thus the final droplet sizes are smaller. By measuring the scattered light intensity e.g. by a multi channel analyzer (MCA) gives information on the original seed particle size. This PHA method has been described in more detail e.g. by Saros et al. (1996) and Dick et al. (2000), and has been used for particle size distribution measurements between 3 – 15 nm in the atmosphere (Wiedensohler et al., 1994; Weber et al., 1995; 1997; 1998) and in the laboratory experiments (Hanson et al., 2002), as well as for the determination of particle chemical composition in the same size range (O'Dowd et al., 2002a; 2004).

In this work, it was recognized that if the final droplet size depends on the seed particle size, then the droplets formed by homogeneous nucleation (without seed particles) should yield the smallest final droplet sizes. This effect allows one to use very high super-saturations since the separation between the unwanted droplets formed by homogeneous nucleation and droplets formed on nanometre-sized seed particles (nano-CN) or clusters can be done. The supersaturation inside the PHA-UCPC condenser can be easily adjusted by varying the temperatures of the saturator and the condenser. Application of the PHA-method down to almost arbitrarily small seed particles is described in detail in **Papers III** and **IV**.

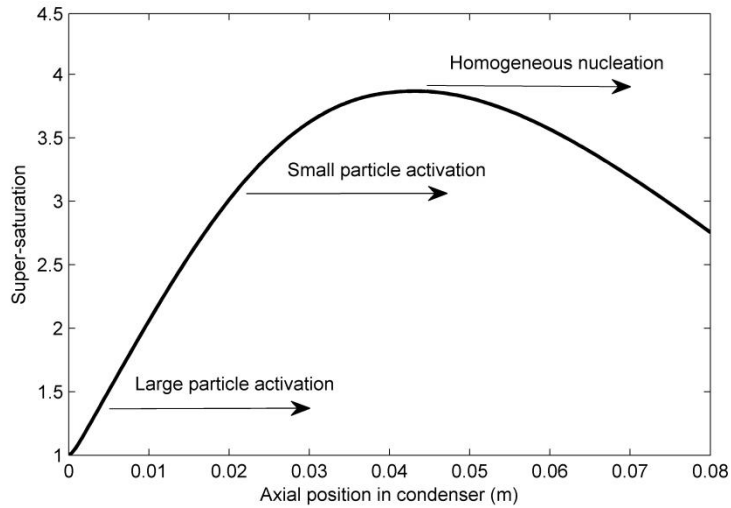


Figure 4. Axial super-saturation profile inside the PHA-UCPC condenser as calculated with Comsol. Due to size and super-saturation dependent activation probabilities, particle growth time and thus final droplet size depend upon seed particle size.

An example of the pulse height distributions in the absence and presence of 1.3 nm seed particles is shown in Fig. 5. The leftmost mode in the pulse height distribution (PHD) results from the homogeneous nucleation, while the rightmost mode represents the droplets formed on large (> 10 nm) particles abundant in the room air. The mode in the middle results from droplets formed via heterogeneous nucleation on those nanometre-sized seed particles. This mode is clearly distinguishable from the mode of homogeneously nucleated droplets and, in principle, the separation can be done.

In practice, the separation between the homogeneous nucleation and cluster – or nano-CN – activation is not straightforward since the atmospheric sub-3 nm particle concentrations are assumed to be relatively small. Therefore, in the field measurements described in **Paper III**, we used a self-constructed diffusion battery where the final stage removed all particles small enough to produce pulse heights overlapping with pulses from homogeneous nucleation. The application of the diffusion battery also offered an independent method to roughly estimate the size of the detected nano-CN.

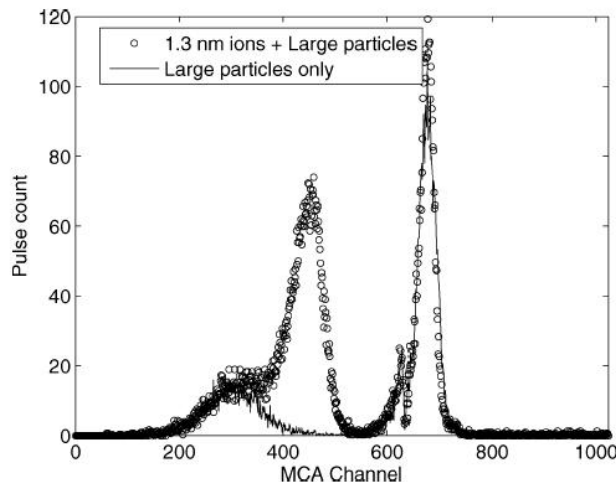


Figure 5. Examples of the pulse height distributions in presence and absence of 1.3 nm calibration ions (**Paper IV**). Large particles present in the aerosol sample accumulate around MCA channel 650. The mode around channel 300 represents homogeneous nucleation of *n*-butanol inside the PHA-UCPC condenser. Pulses in the channels 400-500 result from calibration ions. This mode is clearly distinguishable from the mode resulting from homogeneous nucleation.

One advantage of the PHA-method is that the particle size distribution can be resolved from the PHD. Also the detection efficiency can be accounted for. To do that, the PHA-UCPC transfer functions need to be experimentally determined. The transfer function calibrations and a discussion of data inversion are presented in **Paper IV**. Besides the studies included in this thesis, the presented modified PHA-UCPC has been used in our recent studies for gaining information on atmospheric clusters and initial steps of particle formation in Hyytiälä (Lehtipalo et al., 2009; Lehtipalo et al. 2010a;b) and in Mace Head, Ireland (Lehtipalo, et al., 2010a) as well as under laboratory conditions in the Jülich Plant chamber (Dal Maso et al., 2010), the Finnish Meteorological Institute flow tube (Brus et al., 2010), and the laminar flow tube of Leibniz Institute for Tropospheric Research (IfT), Leipzig (Berndt et al., 2010).

### 2.2.3 Expansion CPC

As discussed above, a rapid adiabatic expansion of a vapour-particle mixture leads to super-saturated conditions and subsequent activation of the particles as the super-

saturated vapour condenses onto the sampled particles. The expansion CPC (E-CPC) used in this work (**Paper III**) was an improved version of the one described by Kürten et al. (2005). Modifications made to the E-CPC during this work comprise automated scanning of the expansion ratio and the use of a diffusion tube system for filtering out sub-3 nm nano-CN in order to be able to measure the onset expansion ratio (related to supersaturation) of homogeneous nucleation. As the condensing vapour, both water and butanol were used. In the E-CPC, the sample flow is mixed with a flow of particle free air saturated with the condensing vapour. This mixture is then directed into an expansion chamber. After an adiabatic expansion, particles within the sample are activated and grow to sizes where they can scatter visible light from a laser beam. The amount of light forward-scattered by the droplets is measured as a function of time. Growing droplets scatter light depending on their size according to the Mie-theory and the concentration of droplets can be calculated from the scattering intensity maxima (Wagner, 1985, Kürten et al., 2005). By scanning the expansion ratio (i.e. the ratio of the initial pressure and the pressure after expansion) and thus changing the super-saturation inside the expansion chamber, we were able to activate particles of different sizes. These expansion scans were performed until the onset of homogeneous nucleation. By screening out the sub-3 nm particles (nano-CN), the onset of homogeneous nucleation could be defined and information from nano-CN concentrations obtained.

#### **2.2.4 Mixing type particle size magnifier (PSM)**

As mentioned earlier, one of the methods used to produce supersaturation is turbulent mixing of a warm saturated air stream with a cool aerosol sample flow (e.g. Kousaka et al., 1982; Okyama et al., 1984). The saturation vapour pressure increases exponentially with temperature; therefore, the total amount of vapour entering the mixer also increases exponentially as a function of saturator temperature. The temperature of the gas after mixing equals the average of temperature of the saturated air flow and the aerosol sample flow, weighted by the relative flow ratios. Similarly, the vapour content after mixing is flow ratio weighted average of the vapour content in the saturator and aerosol flows. Because of the exponential temperature dependence of the saturation vapour pressure, the flow becomes supersaturated due to mixing. Figure 6 shows the saturation vapour pressure of *n*-butanol (Schmeling and Strey, 1983 in Viisanen and Strey, 1994) as a function of temperature. If a saturated flow at a temperature of 330 K is turbulently and adiabatically mixed at a 1:1 ratio with a sample flow maintained at 280 K the



resulting flow temperature after mixing is 305 K. The (partial) vapour pressure of *n*-butanol after the mixing is half of the vapour pressure in the saturator flow. The saturation vapour pressure at 305 K is significantly lower, and thus the gas becomes supersaturated during the mixing process. In reality, of course, the process is not adiabatic and the heat transfer between the gas and the mixer walls affects the achieved supersaturation. Therefore, the geometry and, for example, the heat conductivity and heat capacity of the mixer can significantly affect the performance of the mixer (e.g. Sgro and Fernández de la Mora, 2004). Another possible problem associated with this method is that mixing can never be completely uniform and local supersaturation maxima can occur in the flow field. This effect limits the maximum average supersaturation that can be used in order to avoid homogeneous nucleation in those local hot spots.

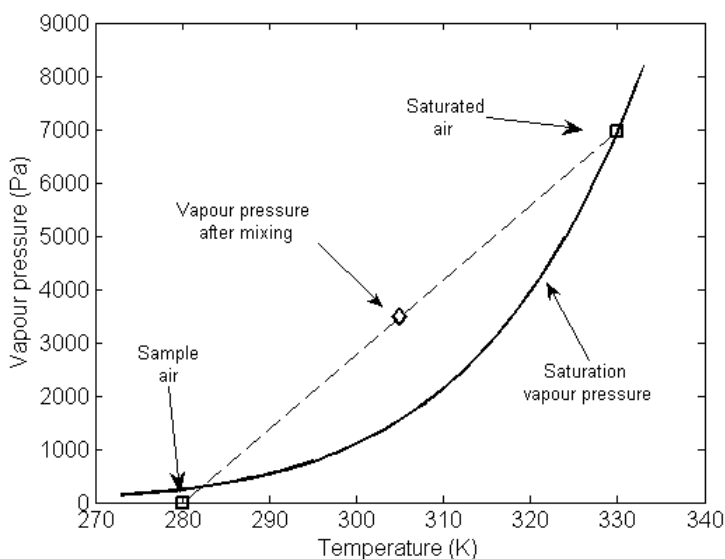


Figure 6. Saturation vapour pressure curve for *n*-butanol. If saturated air at 330 K is adiabatically mixed with the sample air at 280 K (1:1 ratio), the resulting vapour pressure in the mixture exceeds the saturation vapour pressure at the temperature of the mixture. Operation of the PSM is based on this feature.

The particle size magnifier (Vanhanen et al., 2009; 2010) used in **Paper V** of this study is based upon two recent major developments in the field of particle detection. Firstly, the work of Sgro and Fernández de la Mora (2004) (and the references therein) with their development of a mixing type particle size magnifier for almost arbitrarily small particles, and secondly, on the study by Iida et al. (2009) to find the most suitable working fluid to be used in a CPC. The critical dimensions and the

geometry of the present PSM are close to those given by Sgro and Fernández de la Mora (2004). These authors studied different combinations of geometries, flow rates and mixing ratios to optimize the performance of the PSM.

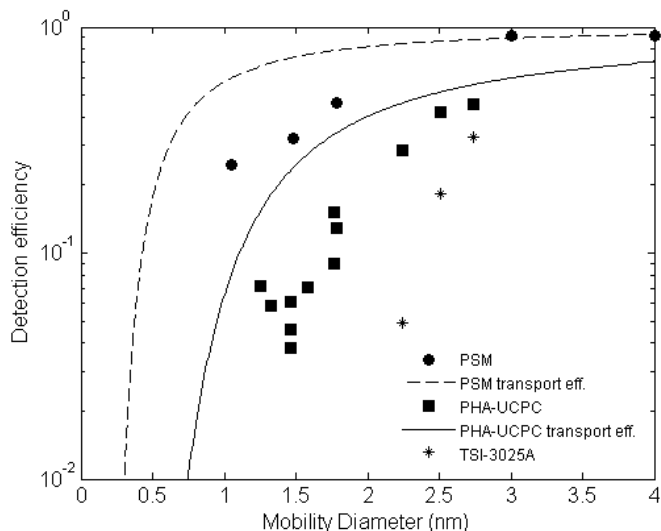


Figure 7. The detection efficiency of the PSM, the raw detection efficiency of the PHA-UCPC and a comparison to state-of-art commercial detector, TSI-3025A. Data comprise calibrations using different test particles and mobility standards discussed in chapter 2.1. The dashed and solid lines depict the calculated (see e.g. Baron and Willeke, 2001) nanoparticle transport efficiencies for the PSM and for the PHA-UCPC, respectively. The transport efficiency determines the theoretical upper limit for detection efficiency assuming a unity activation probability. It should be noted that the detection efficiency in the case of the PHA-UCPC can be accounted for in the PHA-UCPC data inversion.

The choice of the working fluid used in the present PSM is based upon the findings by Iida et al. (2009) that compounds with high surface tension and low saturation vapour pressure efficiently activate nano-CN with a low homogeneous nucleation rate. Therefore, in this work, diethylene glycol, a compound fulfilling those requirements, was used. Diethylene glycol was also experimentally tested by Iida et al. (2009) in the UM-UFCNC prototype (Stolzenburg and McMurry, 1991), showing a superior performance in the sub-2 nm size range. Due to the low vapour pressure of diethylene glycol, particles do not reach optical sizes ( $\sim 1 \mu\text{m}$  in diameter) but grow only up to ca. 100 nm in diameter. Therefore, an external CPC (TSI 3010) is used for detecting the activated particles in this design. Calibration results (Vanhanen et al., 2009; 2010) showed that the present PSM detects charged particles with near unity efficiency down to  $\sim 1.5$  nm (Fig. 7). Below this size,  $\sim 50\%$

of the smallest calibration ions, tetra-methyl-ammonium-ions with a mobility equivalent diameter of 1.05 nm, were still activated in the PSM in comparison to the reference electrometer. Recently, the PSM has been commercialized by Airmodus Ltd. (Airmodus model A-09).

## 2.3 Neutral cluster and Air Ion Spectrometer (NAIS)

One intention of the work presented in this thesis was to test different methods for cluster or nano-CN detection. In the previous chapter, four different CPC techniques were discussed. Here, a completely different approach is presented. The neutral cluster and Air Ion Spectrometer (NAIS, Airel Ltd. Tartu, Estonia; Mirme et al., 2007, Mirme et al., 2009; Asmi et al., 2009) was developed for high time resolution measurements of naturally charged and neutral clusters and particles. The measured mobility range extends from 3.2 to 0.0013 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> corresponding to mobility diameters of 0.8–40 nm in NTP-conditions. The NAIS consists of two identical mobility analysers: one for measuring positive and one for measuring negative ions. The analysers consist of an inner and outer cylinder. The electric field between these cylinders increases in the direction of the flow. The outer cylinder is divided into 21 isolated collector rings. Ions precipitate on these collector rings according to their electrical mobility and the current induced by the particles is measured by electrometers. For neutral particle measurements, the NAIS is equipped with corona chargers. Charger ions interact with sampled aerosol for a well defined time, after which they are filtered by means of a coaxial electric filter ring to prevent any space charge effects in the analyzer. The NAIS operation principles are described in more detail by Mirme et al. (2009).

Measurement of neutral particles by NAIS is based on artificial charging. Charger ions have mobility diameters ranging from less than 1 nm up to ca 1.5 nm in negative polarity and 1.8 nm in positive polarity (Asmi et al., 2009). The size distribution of ions depends on the composition of sample air. The NAIS does not separate between charger generated ions and originally neutral clusters charged via collisions with charger ions. This fact sets the lowest theoretical detection limit for neutral particles around 1.5 – 1.8 nm (Asmi et al., 2009). The NAIS was used during the field measurement campaign described in **Paper II**.

### 3 Field studies

Field studies related to this work were performed during spring 2006 (**Paper II**) and spring 2007 (**Paper III**) at the SMEAR II station (Hari and Kulmala, 2005) in Hyytiälä, Southern Finland. During the first measurement campaign, the UF-02proto and NAIS were used for sub-3 nm particle measurements in conjunction with other aerosol instrumentation (**Paper II**). The second campaign focused on testing the applicability of PHA-UCPC and E-CPC for ambient air studies of nano-CN concentrations (**Paper III**).

The data presented in **Paper II** suggest that below the 3 nm detection limit of ordinary aerosol instrumentation there seems to be a perpetual pool of neutral clusters. The existence of ion clusters in the diameter range from less than 1 nm up to 2 nm has been known for decades and their concentrations have been measured using various types of ion spectrometers (Kulmala and Tammet, 2007). Recent progress in mass-spectrometric techniques has prepared the way for identifying the chemical species involved in the formation and growth of those ion clusters (Eisele, 1986; Eisele, 1989; Junninen et al., 2010; Ehn et al, 2010). However, the application of mass spectrometric techniques for detection of neutral clusters is extremely complicated. Even though the first publications on utilization of MS techniques for neutral cluster detection in laboratory conditions appeared a decade ago (Eisele and Hanson, 2000), the first report where a mass spectrometer was used for identifying the composition of neutral clusters in atmospheric conditions appeared only very recently (Zhao et al., 2010). Thus, the instruments described in this work are valuable tools for obtaining information on the dynamics of sub-3 nm particles.

The persistent pool of clusters is theoretically predicted by Kulmala et al. (2000). Clusters, if activated by sulphuric acid could explain ambient observations of the dependence of the nucleation rate on sulphuric acid concentration (see chapter 4). Thus, the observation of such a population of clusters supports the so called cluster activation theory presented by Kulmala et al. (2006).

The observations by the NAIS and the UF-02proto CPC (**Paper II**) were qualitatively reproduced in the following spring with the PHA-UCPC and the E-CPC (**Paper III**). Both instruments showed that the air in the boreal forest environment of Hyytiälä contained nano-CN with a variable concentration of some thousands up to  $\sim 100\,000\text{ cm}^{-3}$ . An example of the time development of the (neutral cluster) size distribution between 1.2 and 4 nm as measured by the PHA-UCPC

equipped with an ion filter is shown in Figure 8. The same time period is shown as in Figure 1. From Figure 1, it would be impossible to conclude that such a population of nano-CN was persisting in the air. The question that still cannot be satisfactorily answered is the exact role of these nano-CN in atmospheric daytime nucleation events. Since those nano-CN can be activated for growth inside the supersaturated environment of the PHA-UCPC condenser or E-CPC expansion chamber, they could, in principle serve as seeds for heterogeneous nucleation of atmospheric supersaturated vapours as well. Unfortunately, from the data presented in **Paper III**, such conclusions cannot be directly drawn.

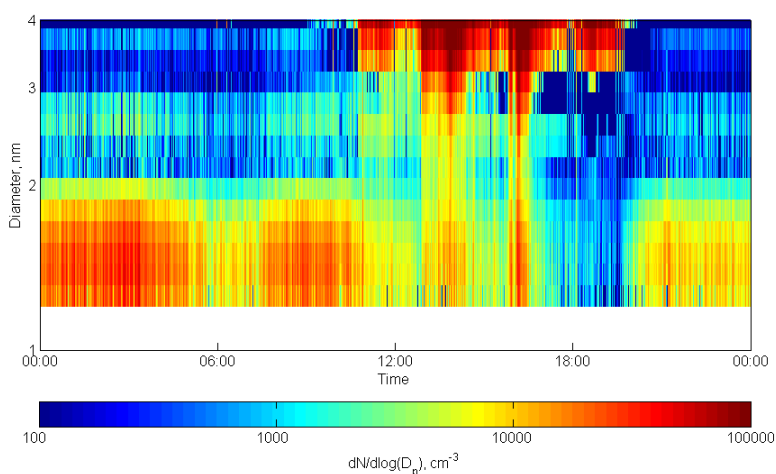


Figure 8. The particle size distribution between 1.3 and 4 nm as measured with PHA-UCPC during the same day as the one presented in Figure 1. The PHA-UCPC technique clearly yields new information on the sub-3 nm particle concentrations.

The data presented in **Paper III** were recently analyzed in more detail (Lehtipalo et al., 2009). The nano-CN concentration estimate reported in the **Paper III** was slightly decreased (to 500 – 50 000 cm<sup>-3</sup>). Also the production rate of those nano-CN via ion – ion recombination was estimated and found to account only for a small fraction of the total production rate. Lehtipalo et al. (2009) also showed that nocturnal formation of nano-CN was frequent. This observation indicates that their origin could be related, for example, in oxidation of certain volatile organic compounds (VOC), accumulating in the surface layer during night time, rather than e.g. clustering of sulphuric acid, which is more abundant in day-time. This conclusion is supported by recent laboratory experiments performed at Leibniz

Institute for Tropospheric Research laminar flow tube (IfT-LFT, Lehtipalo et al., 2010b) showing that ozonolysis of certain alkenes can produce high concentrations of nano-CN detectable with the PHA-UCPC.

The existence of concentrated pool of nano-CN in the boreal forest environment was the primary outcome of the two field studies. Another outcome of the study presented in **Paper II** was that the starting size of atmospheric nucleation seem to be around  $\sim 1.5$  nm. Furthermore, in **Paper II**, it was shown that neutral nucleation dominates over the ion-induced mechanism. In comparison to neutral particles, the heterogenous nucleation on charged particles is assumed to be energetically favoured (Winkler et al., 2008a) and it has been suggested that the ion mediated mechanism could explain a significant fraction of the observed nucleation rates in Hyytiälä (Yu and Turco, 2008). Our observation about the dominance of the neutral pathway, supported by later studies by Manninen et al. (2009), and Kulmala et al. (2010) adds to the ongoing debate related to connection between galactic cosmic radiation and climate via ion-induced nucleation (Svensmark et al., 1997; Kirkby, 2007; Duplissy et al., 2010; Kulmala et al., 2010).

Even though the results from the field studies yielded significant new information, the question about the details of the nucleation mechanism still remain open. In the following section, the lessons learned about the nano-CN detection were applied in a laboratory nucleation experiment.

## 4 Laboratory experiments on sulphuric acid nucleation

Even though atmospheric observations suggest that nucleation takes readily place in presence of sulphuric acid with concentration above  $10^5 - 10^6$  molecules  $\text{cm}^{-3}$  (Weber et al., 1996; Birmili et al., 2003; Sihto et al., 2006; Riipinen et al., 2007; Kuang et al., 2008; Paasonen et al., 2010), laboratory experiments performed in flow tubes have systematically failed to reproduce nucleation rates ( $J$ ) as high as those detected in the atmosphere (Wyslouzil et al., 1991; Viisanen et al., 1997; Ball et al., 1999; Zhang et al., 2004; Berndt et al., 2005; 2006; 2008; Young et al., 2008; Benson et al., 2008; Brus et al., 2010). In those experiments, both the onset concentration of sulphuric acid (concentration required to produce unit  $J$ ) and the “slope”  $d(\log J)/d(\log[\text{H}_2\text{SO}_4])$ , that should give the number of sulphuric acid molecules in a critical cluster (Kaschiev et al., 1982), have shown significant

divergence from atmospheric observations (Fig. 9). Different experiments have also yielded significantly differing results. Those results suggest that nucleation in sulphuric acid – water system is not efficient enough to explain ambient values of  $J$ , and yielded proposals that e.g. ammonia (Ball et al., 1999) or organics (Zhang et al., 2004) were participating in nucleation. Closest to the atmospheric data has been the data reported by Berndt et al. (2005) who produced sulphuric acid in-situ via reaction of OH and SO<sub>2</sub> in the reactor. Due to this observation, it was suggested that possibly some other sulphur containing compounds, e.g. HSO<sub>5</sub>, formed in the subsequent steps in the reaction chain starting from OH + SO<sub>2</sub>, were driving nucleation (Friend et al., 1980; Berndt et al., 2008; Laaksonen et al., 2008). In this work, it was recognized that the experiment by Berndt et al. (2005) differed from the previous studies also in the way that it was the only experiment in which sulphuric acid was produced continuously in the flow tube, and for a relatively long time compared to other experiments. This difference was found to be one of the main reasons for the apparent disagreement of different laboratory and ambient data as will be discussed further below.

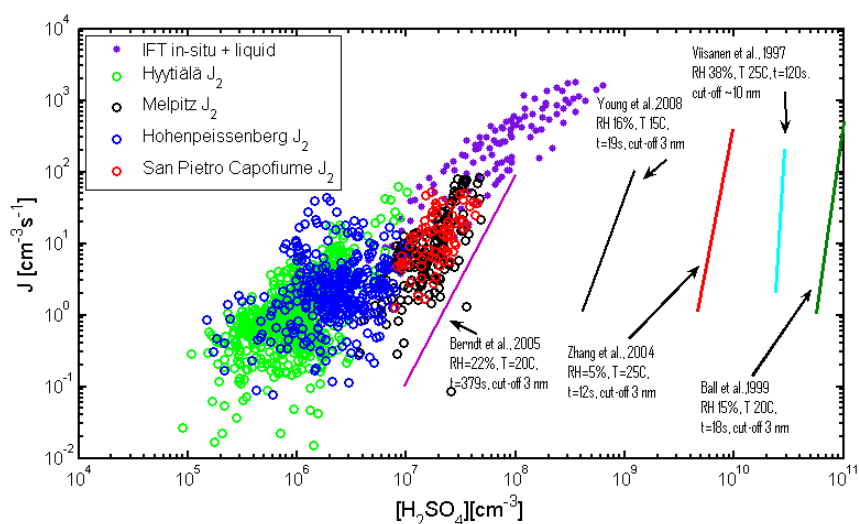


Figure 9. Nucleation rates as a function of sulphuric acid concentration as observed in the atmosphere (data adopted from Paasonen et al., 2010) and in different laboratory experiments. Results from the present work (IFT in-situ + liquid) match the ambient data while all earlier studies have yielded higher onset sulphuric acid concentrations and higher slopes. The reason for smaller divergence of the Berndt et al. (2005) data is that they used ~10 times longer residence time compared to other studies and produced sulphuric acid *continuously* in-situ in the flow tube. Therefore, the particle growth to the measurement regime of the CPC has been much more efficient. Residence times, nominal D50 size of the CPC and experimental conditions used in previous experiments are given in the figure.

The laboratory study presented in the **Paper V** was carried out in Leibniz Institute for Tropospheric Research laminar flow tube (IfT-LFT) with an inner diameter of 8 cm and total length of 5.05 m. A 3.44 m long middle section of the tube is equipped with UV-lamps for continuous photochemical sulphuric acid production. Sulphuric acid can also be introduced in the tube by passing a fraction of carrier gas flow through a saturator containing pure sulphuric acid, maintained at 15°C temperature to suppress the evaporation. High purity (99.9999999%) synthetic air served as the carrier gas.

Sulphuric acid concentrations were measured by a chemical ionization mass spectrometer (CI-MS; Eisele and Tanner, 1993; Petäjä et al., 2009). Results were compared to the output of a kinetic model (Berndt. et al., 2006) and to the total sulphate concentration determined by a denuder – ion chromatograph system. Particle concentrations were measured with the PHA-UCPC and the PSM together with a commercial TSI-3025A CPC. To determine the concentrations of unavoidable organic contaminants in the system, a proton transfer reaction mass spectrometer (PTR-MS, Hansel et al., 1998) was used. No measurable quantities of organics were detected. Also ammonia concentrations were below the detection limit of the applied Omnisens TGA 310 trace gas analyzer. The detection limits are, however, such high (0.1ppb for ammonia, and several ppts for a single organic mass) that even though no signal from those unwanted impurities were detected, their presence and role in nucleation cannot be excluded.

The results of the laboratory study are presented in Fig. 9 together with ambient data from four European stations (Paasonen et al., 2010). Lines in the figure depict the results from previous laboratory studies. The data of the present work coincides with the atmospheric data, while shows a divergence from earlier flow tube experiments.

In **Paper V**, it is speculated that the differences between the experiments result from differences in experimental systems, mainly residence time and the performance of the particle detector. Growth due to sulphuric acid condensation in close atmospheric  $[H_2SO_4]$  is a very slow process (Kulmala, 1988; Lehtinen and Kulmala, 2003; Nieminen et al., 2010). Thus, the particles do not easily reach the detectable size within the short residence times used unless the sulphuric acid concentration is far above the atmospheric range of  $10^5 - 10^8$  molecules  $cm^{-3}$ . This fact could explain, in part, the disagreement between ambient and laboratory data. With a combination of laboratory experiments and fluid and aerosol dynamical modelling this can be shown to be possible (Sipilä et al., 2010).



Fig. 10 shows, as a result of a modelling study (Sipilä et al., 2010), an example of the particle size distributions at the outlet of the IFT-LFT after a 379 second residence time using sulphuric acid from the liquid saturator. Diameters in Fig. 10 are geometric diameters. Assuming activation nucleation with  $J = 3 \cdot 10^{-6} \text{ s}^{-1} [\text{H}_2\text{SO}_4]^1$  (see e.g. Riipinen et al, 2007 and **Paper V**), collision limited sulphuric acid condensation (Nieminen et al., 2010) and the detection efficiency curve of a TSI-3025 CPC (Sem, 2002) with a D50 diameter of approximately 3 nm, only a tiny,  $[\text{H}_2\text{SO}_4]$  dependent fraction of the total size distribution can be counted.

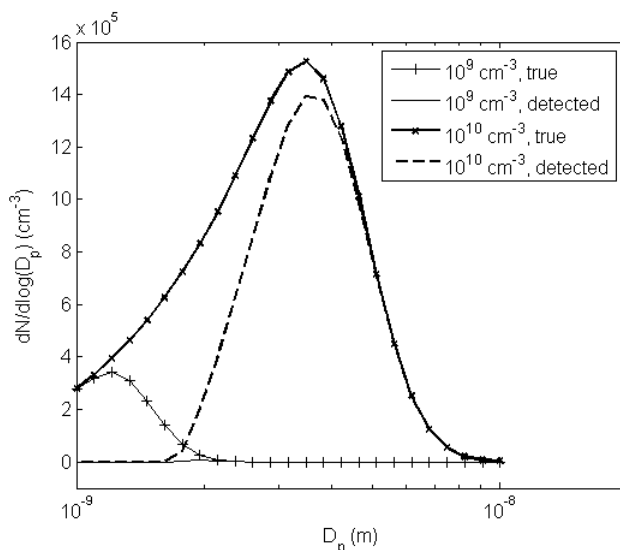


Figure 10. The simulated particle size distribution at the output of IFT-LFT with a total residence time of 379 seconds, together with the fraction of the size distribution that can be detected assuming TSI-3025A CPC detection efficiency curve (Sem, 2002). The nucleation rate is expressed as  $J = 3 \cdot 10^{-6} \text{ s}^{-1} [\text{H}_2\text{SO}_4]^1$  and growth is assumed to result from pure sulphuric acid condensation.

To test the model, the output of the simulations were compared to the experimental data measured using TSI-3025 CPC as a detector (Berndt et al., 2007). The model predicts the measured particle number concentration reasonably well (Fig. 11). This shows that the nucleation experiments in which the size sensitive particle counting is not taken into account might suffer from serious undercounting, affecting both the apparent onset  $[\text{H}_2\text{SO}_4]$  and the slope. Since in many studies the measured number concentration is converted into a nucleation rate by simply dividing by the estimated nucleation time, the effect shown in Fig. 11 is directly transferred to conclusions about the nucleation rate – sulphuric acid concentration relation. A

more detailed discussion can be found from supplementary online material of **Paper V** (<http://www.sciencemag.org/cgi/content/full/327/5970/1243/DC1>).

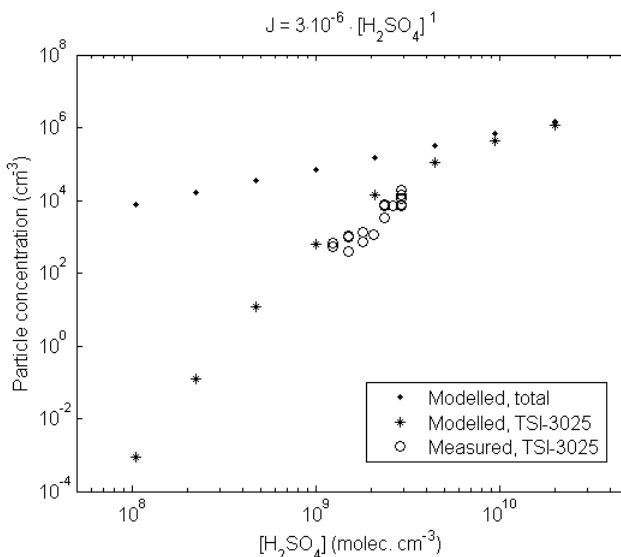


Figure 11. Comparison of particle number concentration at the outlet of IfT-LFT as predicted by the model (stars) to the measured number concentration (circles). The nucleation rate is described in this case by  $J = 3 \cdot 10^{-6} \text{ s}^{-1} [\text{H}_2\text{SO}_4]^1$ . Note that the use of the measured concentration to determine the nucleation rate will result in an error since the true number concentration is significantly higher (dots).

One of the key findings of the present laboratory study was that sulphuric acid, not any other sulphurous species, drives the nucleation. Existing atmospheric data show the connection between sulphuric acid and nucleation rate as discussed earlier. However, the study presented in **Paper V** is the first one showing the cause and effect relationship between these two. Since sulphuric acid is formed in the atmosphere mainly from the reaction of  $\text{SO}_2$  with  $\text{OH}$ , it could have been possible that some other compounds reacting with  $\text{OH}$  were responsible for nucleation. On the other hand,  $\text{OH}$  is produced mainly via photolysis of ozone (Rohrer and Berresheim, 2006) and thus, eventually, the common nominator between nucleation rates and sulphuric acid concentrations could be the sun radiation intensity.

The results presented in Fig. 9 and **Paper V** indicate that sulphuric acid is most probably the limiting factor in atmospheric nucleation. If the atmospheric observations can be reproduced in a clean environment of IfT-LFT, the possible, still unknown, stabilizing agent should be abundant in any natural environment and the nucleation rate should not be very sensitive to the concentration of that

compound. If only sulphuric acid is considered, parameterization of nucleation in global models would be straightforward (Spracklen et al., 2006). However, more work – both experimental and theoretical – including e.g. RH (Berndt et al., 2010) and temperature dependence, is required before the observations reported in **Paper V** can be utilized in global climate models.

## 5 Review of papers

**Paper I** presents the results of the calibration experiment performed for the tuned UF-02proto CPC. This was the first successful experiment in which we were able to measure particles below 3 nm and even 2 nm in diameter under laboratory conditions.

**Paper II** describes the results from the field campaign in which UF-02proto CPCs described in the Paper I were used in conjunction with another newly developed detector, neutral cluster and air ion spectrometer (NAIS). Key findings of this paper are that in boreal forest environment, there seems to exist a numerous pool of neutral nanometre sized clusters that potentially can participate in the atmospheric new particle formation, that atmospheric nucleation occurs at <2nm sizes, and that neutral nucleation dominates the particle formation over the ion induced mechanisms.

**Paper III** describes the method that allows one to use very high butanol supersaturations, and thus improve the detection efficiency of the ultrafine condensation particle counter for sub-3nm particles. In this paper, the first results from the field measurements with the PHA-UCPC and the E-CPC are also reported. Confirming the observations first reported in the Paper II, the main outcome of the study is that, in boreal forest environment, there is a numerous population of neutral nano-sized condensation nuclei that can be activated in a supersaturated vapour.

**Paper IV** reports the results from the laboratory calibration experiments for the pulse height analysing ultrafine condensation particle counter that was used in the field experiments reported in Paper III, and in the laboratory study presented in Paper V. In this paper, the data inversion to convert the measured pulse height distributions to particle size distribution is also discussed.

**Paper V** summarizes our findings on sulphuric acid nucleation. In this paper, the knowledge and understanding of nano-particle and cluster detection together with well established reactor and state-of-art precursor detectors yielded new insight into the nucleation process. In this paper, we show that sulphuric acid is the key in the mystery of atmospheric nucleation.

## 6 Author's contributions

I am solely responsible for the summary part of this thesis. In **Paper I**, I performed the tuning of the UF-02 proto CPC and all calibration experiments, as well as participated in the data processing and writing. In **Paper II**, I performed the UF-02 proto CPC tuning and calibration experiments, participated in the measurement campaign in SMEAR II station, contributed to data processing, and wrote some technical parts of the text. In **Paper III**, I recognized that pulse height analysis can be used to distinguish between homogeneous and heterogeneous nucleation, developed the methods for the application of this pulse height analysis technique to measure sub-3 nm particles and designed the improvements, including supersaturation scanning and diffusion filter for nano-CN, done to the E-CPC. I performed most of the laboratory tests for the instruments and participated in the field campaign in SMEAR II station. I performed the most of the data analysis and wrote the article. In **Paper IV**, I performed the tuning of the PHA-UCPC and calibration experiments together with my co-authors, participated in the data analysis and discussions about data inversion, and wrote the paper. In **Paper V**, I acted in combining the scientific expertise and instruments used in the study. I participated in the design of the laboratory experiments in IfT. I performed the laboratory experiments in IfT together with my co-workers, contributed to the design and development of the PSM, performed the additional calibration experiments for the PHA-UCPC, processed and analysed most of the data from IfT, contributed to the interpretation of the results and wrote most of the text.

## 7 Conclusions

In the work presented in this thesis, the mystery of atmospheric nucleation was approached by the developing methods for direct measurement of newly formed clusters immediately after nucleation. The four condensation particle counters

developed and/or used in this work were all capable to detect particles below 2 nm in diameter. This is a significant step toward direct measurement of atmospheric nucleation, since formerly only particles above 3 nm in diameter could be counted. The results presented in this thesis reveal that particle activation down to close-molecular sizes happens before the onset of homogeneous nucleation, and with proper methods the unwanted disturbance from homogenous nucleation can be avoided. Moreover, the superior performance of the PSM, developed and used in the study described in **Paper V**, showed that with a proper design and choice of working fluid, close-to-unity detection efficiency can be achieved down to at least ~1.5 nm in diameter.

In the field experiments, the concentrations and variation of concentration of nano-CN in the size range from ~1.5 to 3 nm was measured for the first time. Experiments performed in the field showed that, at least in the boreal forest environment, there persists a population of neutral nanometre sized condensation nuclei. These nano-CN could participate in the daytime nucleation events as seeds for heterogeneous nucleation of, for example, sulphuric acid. At this stage, however, their exact role in atmospheric nucleation is still in part an open question, even though our results have recently become more quantitative (Lehtipalo et al., 2009;2010a;b). Results from those field measurements showed that with the present equipment the direct measurement of atmospheric nucleation is possible, though the accuracy can always be improved.

Previous atmospheric observations have already shown the correlation between sulphuric acid concentration and nucleation rate. In this thesis, as a result of laboratory experiments, it was shown for the first time that the correlation is due to a cause and effect relationship and that sulphuric acid, not any other product from OH+SO<sub>2</sub> reaction, is the key species in atmospheric nucleation. It was shown that nucleation of sulphuric acid at atmospheric concentrations can explain the nucleation rates observed in the atmosphere in absence of measurable quantities of unknown contaminants. The reason for the divergence of the results from previous studies was shown to be connected to inefficient growth of freshly nucleated particles and use of improper detectors in the earlier experiments. The results indicate that in presence of sulphuric acid at atmospheric concentrations a numerous population of tiny clusters is readily produced. In the laboratory experiment (**Paper V**) those clusters continued their growth by sulphuric acid condensation (plausibly with co-condensing water). In the atmosphere – containing a variety of different low volatile compounds – those clusters could be activated for further growth by e.g. some organics. Even though gaps in our knowledge about nucleation still remain, these findings add greatly to our understanding of nucleation as well as of the role

of anthropogenic pollutant emissions (especially SO<sub>2</sub>; Arneth et al., 2009) in new particle formation and, in turn, climate.

To summarize, in this thesis new methods and instrumentation to detect particles of close molecular sizes were developed and tested. Those methods were utilized in atmospheric measurements as well as in a series of laboratory experiments in a H<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O system. Atmospheric results showed the existence of a persistent pool of neutral nanometre sized condensation nuclei or clusters. In ambient studies, though, numerous variables affect the particle concentrations and dynamics and thus the exact nucleation mechanism could not be resolved. In the laboratory system – with no interference from those numerous disturbing factors, and with a steady state situation and highly reproducible experimental conditions – the developed instrumental techniques showed their power, truly opening new insights into atmospheric nucleation.

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