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**A review of Ion
Induced Nucleation**

M. B. Enghoff and H.
Svensmark

The role of atmospheric ions in aerosol nucleation – a review

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Abstract

Atmospheric aerosols affect climate and yet the reason for many observed events of new aerosol formation is not understood. One of the theories put forward to explain these events is that the presence of ions can enhance the formation of aerosols. The theory is called Ion Induced Nucleation and in this paper the state of observations, theory and experiments within the field will be reviewed. While evidence for Ion Induced Nucleation is accumulating the exact mechanism is still not known and more research is required to understand and quantify the effect.

1 Introduction

Aerosols are present throughout the atmosphere and affect Earth's climate directly through backscattering of sunlight and indirectly by altering cloud properties (Forster et al., 2007). However the exact mechanism controlling the early stages of aerosol formation is still not understood. Several measurements of atmospheric nucleation have been reported where the observed nucleation rates cannot be explained by the traditional theory of binary homogeneous nucleation by water and sulphuric acid (Hoppel et al., 1994; Weber et al., 1996; Weber et al., 1997; Clarke et al., 1998; O'Dowd et al., 1999; Weber et al., 2001; Birmili et al., 2003). A ternary nucleating agent such as ammonia has been proposed to enhance the nucleation process by stabilising early cluster formation (Weber et al., 1996; O'Dowd et al., 1999; Weber et al., 1998; Kulmala et al., 2000). Another possibility is that ions, produced mainly by galactic cosmic rays, can explain the observed nucleation rates (Turco et al., 1998).

In 1895 it was shown for the first time that ionising radiation in the form of x-rays has an impact on the nucleation of particles in the gas phase (Wilson, 1895). Using an expansion chamber the Scottish scientist Wilson noted that the amount of droplets formed was greatly enhanced when the experiment was exposed to x-rays. Later the experiment was repeated with radiation from Uranium with the same result and it was

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concluded that the droplets were formed on ions (Wilson, 1899). With time other experiments have shown similar effects under conditions with extreme gas compositions or ionisation levels (Megaw and Wiffen, 1961; Bricard et al., 1968; Vohra et al., 1984; Raes et al., 1985; Rabeony and Mirabel, 1987; Adachi et al., 1992; Kim et al., 1997), and in normal atmospheric conditions (Svensmark et al., 2007).

Dickinson (1975) speculated on how ions can influence aerosol nucleation and clouds; later Arnold (1980) suggested that multi ion complexes can serve as condensation nuclei in the stratosphere, and Turco et al. (1998) argued that the recombination of ions could nucleate aerosols. In 1997 the role of ionisation from galactic cosmic rays was linked with cloud formation based on satellite observations of clouds and ground based cosmic ray measurements (Svensmark and Friis-Christensen, 1997; Marsh and Svensmark, 2003). A similar connection was later discovered by Harrison and Stephenson (2006) for the UK and Udelhofen and Cess (2001) found that cloud cover in the United States for the last 100 years correlated with solar activity. Kazil et al. (2006) modelled the response in cloud cover forced by cosmic ray changes but found no significant effect.

Since the amount of atmospheric ions is changing on timescales of hours to millennia a connection between ions and clouds could result in corresponding changes to aerosol and cloud properties which would be important for understanding past and even future climate changes.

In this paper the role of ions in aerosol nucleation will be reviewed – for a more general review of aerosol nucleation see the book by Seinfeld and Pandis (1998, Chap. 10) or the recent paper by Curtius (2006). Three areas: Observations, Theory and Experiments will be described in separate sections. Observations (Sect. 2) covers all measurements performed in the atmosphere from studies of the general behaviour of ions to particle nucleation observations where the role of ions is considered. In Sect. (3): Theory, the various equations and models applied to understanding nucleation via ions are presented, and the Experiments section (Sect. 4) describes laboratory measurements from nucleation events to investigations of single reactions. Finally the state of

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the field will be summarised (Sect. 5).

2 Observations

There are numerous studies where atmospheric nucleation rates are reported. A review paper by [Kulmala et al. \(2004b\)](#) lists more than 100 individual investigations several of which report nucleation rates unexplainable by the standard theory of binary homogeneous nucleation. An analysis by [Yu et al. \(2007a\)](#) showed that most of these observations could be described by nucleation by ions (see Sect. 3). Studies where the role of ions is investigated are somewhat more sparse and apply varying methods. However they can be roughly divided into two types - those that solely investigate the behaviour of the ions and those where the development of ions is studied together with nucleation events.

2.1 Ions

An introduction to ion chemistry in the atmosphere has been written by [Ferguson et al. \(1979, Chap. 2\)](#), and [Viggiano \(1993\)](#) has made a description of the instrumentation used for measuring atmospheric ions. A review of atmospheric ion formation and different mechanisms for nucleation via ions was given by [Harrison \(2000\)](#).

Large positive cluster ions ($\text{mass} \leq 2500 \text{ amu}$) were detected in the upper troposphere for the first time in 2002 ([Eichkorn et al., 2002](#)) using a large ion mass spectrometer. The most common ions measured were composed of water, acetone and a proton. Two larger modes were also detected. The lesser of these could be explained by the uptake of sulphuric acid but there were insufficient amounts of condensable gases to explain the largest measured particles by any other means than attachment of small aerosols to the ion clusters. The required concentration of these aerosols was $2.5 \cdot 10^4 \text{ cm}^{-3}$ and their presence could not be explained by homogeneous nucleation, which strongly indicated that the ions participated in the formation. Even larger ions

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with a mass up to 8500 amu were detected directly in the exhaust of a jet aeroplane (Eichkorn et al., 2002). These ions were found to participate in the formation of larger aerosols and might evolve into cloud condensation nuclei (Yu and Turco, 1999).

Many years of work on ions in the free troposphere and stratosphere was summarised by Arnold (2006), and major cluster ions were reported containing sulphuric acid, nitric acid, acetone, water and acetonitrile. Arnold concluded that nucleation via ions, henceforth referred to as ion induced nucleation (INU) can occur in the upper troposphere and that the freshly nucleated particles can be transported either downwards to serve as cloud condensation nuclei or upwards to the stratospheric aerosol layer (the Junge Layer).

Hörrak et al. (1998a) described how the measurement of ion mobility in air can be used to determine the size of the ion. That technique has recently been used to detect a pre-existing distribution of neutral aerosols below the limit of detection by conventional aerosol sizing techniques – the measurement was achieved by first ionising the neutral particles and then measuring the mobility of the resulting ions (Kulmala et al., 2007). Hörrak et al. (1998b) used an air ion spectrometer to measure bursts of intermediate ions with mobilities from 0.034 to 0.5 cm²V⁻¹s⁻¹ corresponding to sizes of 1.6 to 7.4 nm at Takhuse, Estonia. These bursts could either be explained by a) attachment of ions to homogeneously nucleated particles or b) INU. The observed bursts were however smaller than what would be expected for homogeneous nucleation.

The ion production rate Q is a key parameter for any theory of INU since it will determine the amount of ions available for nucleation. Laakso et al. (2004b) compared two methods of estimating Q : 1) Direct measurement of ionisation sources (Radon, galactic cosmic rays and gamma radiation from the ground); and 2) Measuring the distributions of small ions and particles and then solving Eq. (1) for Q assuming steady-state.

$$\frac{dn_{\pm}}{dt} = Q - \alpha n_{\pm}^2 - n_{\pm} \int_{d_p} \sum_{q=-\infty}^{\infty} \beta_{\pm}(d_p, q) N(d_p, q) dd_p \quad (1)$$

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where the second term in Eq. (1) is the loss of ions by recombination and the third term corresponds to the attachment of small ions to aerosols. n_{\pm} is the concentration of either negative or positive ions (assumed to be equal), α is the ion-ion recombination coefficient, d_p is the aerosol diameter, q the charge of the aerosol particle, $\beta_{\pm}(d_p, q)$ the ion-aerosol attachment coefficient and $N(d_p, q)$ the aerosol concentration. Since the recombination and attachment coefficients are known, and the concentrations of ions and aerosols measured, it is possible to estimate Q . This method did however underestimate the ion production rate somewhat compared to the direct method (2.6 ion pairs cm^{-3} vs 4.5 ion pairs cm^{-3} for the conditions in this setup), possibly due to the lack of information about aerosol particles smaller than 3 nm. The measurements were taken during the QUEST campaign in a forest at Hyytiälä, Finland, just above ground level. The research station at Hyytiälä was described by [Hari and Kulmala \(2005\)](#).

2.2 Nucleation

The QUEST campaign also produced a set of simultaneous measurements of aerosol and ion concentrations along with the trace gases sulphuric acid and ammonia ([Laakso et al., 2004a](#)). The particles formed during a nucleation event were overcharged with negative ions indicating the participation of negative ion chemistry in the nucleation process. However little change in the number of small cluster ions (stable ions with a diameter of ~ 1.5 nm) was observed during the events, contrary to what would be expected from INU. This was possibly due to mixing of air parcels or a decrease in the ion condensation sink to other particles previous to the events. Modelling of the observed events indicated that they could be explained mainly by nucleation of sulphuric acid and ammonia with subsequent growth via sulphuric acid and organics and that the ions played a secondary role. A later and more detailed analysis ([Vana et al., 2006](#)) divided the observed nucleations events into strong and weak events based on the amount of nucleated particles, and it was shown by analysis of the charged fraction that ions played the largest role in the weak nucleation events.

Three years of simultaneous ion and particle measurements were reported by [Hir-](#)

sikko et al. (2007a). Ions with sizes from 0.42 to 7 nm were measured along with particles above 3 nm. Each day of measurements were classified as an event, undefined, or non-event day –26% of the days were event days for negative ions while there were 22% event days for positive ions. Intermediate ions (with sizes from ~1.6 nm to 7 nm) appeared during rain- and snowfall possibly due to the breakup of water droplets and the presence of ice crystals, respectively.

In an earlier study from 2001 (Harrison and Aplin, 2001) an attempt was made to directly observe the effect of ions on condensation nuclei in a field study near Reading, England. Two separate Geiger counters were used to identify periods of cosmic ray showers and separate them from other more local ionisation events. A Gerdien counter (Aplin and Harrion, 2000; Gerdien, 1905) measured the negative ions, and aerosols were measured simultaneously. During a 1-hour period with many cosmic ray shower events a positive correlation ($r=0.5456$) was seen between the negative ions and the rate of change in aerosols. If the aerosols were produced by other means than INU (e.g. particles nucleated by another mechanism elsewhere and transported to the sampling site by advection) a decrease in small ions measured by the Gerdien would be expected from Eq. (1) whereas an INU event is characterised by an increase in ionisation followed by an increase in particle concentration. During the same period the aerosol amount did not correlate with wind speed, further indicating that advection did not interfere.

Another series of ground level observations was carried out from March to September 2004, and May to October 2005, near Boulder, Colorado USA (Iida et al., 2006). Aerosol size distributions were measured from 3 nm to 5 μm using a nano- and a regular Scanning Mobility Particle Sizer (SMPS) and an optical particle counter. In addition the mobility of ions corresponding to a size range of 0.4 to 6.3 nm was recorded using a mobility analyser. By operating the nano-SMPS in two modes, with and without the air passing through a charger, it was possible to determine the fraction of charged particles. This was double-checked by comparison with the ratio of ions as measured by the mobility analyser to the total particle number from the nano-SMPS in the overlapping

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size-region. A theoretical analysis showed that for the measured particle growth rates the charged fraction of nucleated particles would retain their original charge. Since most nucleation events showed charged fractions below the expected steady state values it was concluded that INU was not contributing significantly to nucleation. However, a few events showed charge imbalances (mostly with increased negative charge) which could only be explained by INU. A quantitative study showed that the average contribution of INU was about 0.5%.

Laakso et al. (2007) developed an instrument to measure the charged fraction of particles in nucleation events. Particles were passed through a charger that could be turned on and off, and the size distribution was then determined by a differential mobility particle sizer with a switchable polarity to measure either positive or negative ions. Thirty-four particle nucleation events from Hyytiälä forest, Finland, were analysed, and a charged fraction above the expected equilibrium was detected in many cases indicating a contribution from INU. Negative overcharging was more common than positive. It was concluded that INU took place but that neutral nucleation was dominant on most days. That INU is not dominant on this measurement location is also supported by Kulmala et al. (2007). These conclusions are however undergoing debate due to uncertainty in the interpretation of the overcharge of the measured particles (Yu et al., 2007b,c).

Looking at measurements from the same site Kulmala et al. (2004a) discovered that the growth rate of aerosols between 1.5 and 20 nm increases with size. This could be due to the activation of organic vapours meaning that when these are present INU is not dominating for the growth of the aerosol but can still be important for nucleation.

Charged fractions were also measured at three sites in the Baltic Sea region (Kompula et al., 2007), but these indicated that INU was not a major contributor to the observed nucleation events. Simultaneous measurements of ions and particles have additionally been made by the same group at such diverse locations as indoors/outdoors in urban Helsinki (Hirsikko et al., 2007b), along a roadside (Tiitta et al., 2007), in a cloud (Lihavainen et al., 2007), along the Trans-Siberian rail road (Vartiainen et al.,

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2007) and in Antarctica (Virkkula et al., 2007). A special issue of “Boreal Environment Research” was dedicated to air ions and aerosols, dealing with, amongst others, the papers mentioned in this paragraph (Kulmala and Tammet, 2007).

5 Observations in the upper atmosphere are more rare but one set was provided by Lee et al. (2003) who carried out 56 aircraft flights from 7 to 21 km at latitudes between 10°N to 90°N, measuring particle size distributions between 4 and 2000 nm as well as OH and SO₂ concentrations. Backward trajectory calculations supplied information on exposure of the air parcel to sunlight. The data was analysed using a thermodynamic model for INU (Lovejoy et al., 2004) – the model will be described in the Theory section.
10 Two case studies of high and low particle concentrations were presented and modelled successfully by the INU model.

The observational studies approach INU from different angles, and the conclusions are not always clear. Techniques to quantify the importance of INU in observations exist but the debate on how to interpret the data is still ongoing. The main reason for this is that the exact mechanism for INU is not yet known: thus it is difficult to point out which
15 parameters are most important to measure and how to interpret them. One approach to solving this problem is by theoretical analysis, and the next section summarises the various theories and models in the field.

3 Theory

20 Nucleation is basically a competition between the growth and evaporation of molecular clusters. For a stable cluster to be formed an initial energy barrier must be overcome – this barrier is due to the surface tension of the cluster. The height of this barrier is determined by the temperature and concentration of the nucleating species. There are several good introductions to nucleation theory (Seinfeld and Pandis, 1998, Chap.
25 10); (Curtius, 2006). This section will deal with how the addition of an electrical charge alters the nucleation process.

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3.1 Thermodynamic theory

The classical approach to bi-molecular homogeneous nucleation uses thermodynamics, where the standard nucleation rate J (new particles formed per volume per time unit) is defined as:

$$5 \quad J = C e^{\frac{-\Delta G^*}{kT}} \quad (2)$$

where ΔG^* is the free energy of formation of the critical cluster (the required cluster size to overcome the energy barrier), k Boltzmann's constant, T the temperature, and C the pre-exponential factor that can be calculated in various ways, e.g. [Hamill et al. \(1982\)](#)

$$10 \quad C = 4\pi r^{*2} \beta_a N_b \quad (3)$$

where r^* is the radius of the critical cluster. β_a is the collision rate of a molecules (per unit area) and N_b is the concentration of b molecules. The dependency of ΔG on the particle radius can be seen as the red curve in Fig. 1; ΔG^* is the height of the barrier.

The introduction of an ion does, however, change this as a stable equilibrium state (r^s) is introduced prior to the barrier, see the blue curve in Fig. 1. The result is that the energy needed to nucleate is the difference between that of the stable equilibrium (r^s) and that of the unstable where the ΔG function is at a maximum (r^u). Equation (2) is thus changed into:

$$15 \quad J = C e^{\frac{-\delta\Delta G_i}{kT}} \quad (4)$$

20 where r^* in Eq. (3) is changed into r^u (the critical radius for the ion cluster) and N_b to N_j , the ion concentration. ΔG_j is smaller than ΔG^* due to the contribution to the free energy of the electrostatic attraction the ion exerts on the cluster.

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For the classical determination of r^u , r^s and ΔG_i see the work by [Yue \(1979\)](#). [Fisenko et al. \(2005\)](#) investigated the effect of the dipole moment on $\delta\Delta G_i$ and also considered possible explanations for sign preference. [Nadykto and Yu \(2004\)](#) discussed the modelling of the dipole further, and their calculations compared well with experimental nucleation measurements. Thomsons's charged liquid drop model, employed in the determination of $\delta\Delta G_i$, was tested experimentally for various clusters ([Holland and Castlemann Jr., 1982](#)) with a positive core ion. The results compared favourably for water clusters but not for the other ligands tested. Modifications to the model were discussed but these did not resolve the discrepancies. [Yu \(2005\)](#) proposed a modified Thomson model taking into account the interaction between the core ion and the ligand dipoles. For small clusters (with the number of ligands being below 6) the modified theory provided good results for the ligands H_2O , NH_3 , CH_3OH and $\text{C}_5\text{H}_5\text{N}$. The core ion was H^+ in all cases.

It is important to note that the maximum in ΔG only occurs when the gas-phase is saturated with regard to the nucleating compounds, and at sufficiently high supersaturations the energy barrier can disappear completely. Under conditions where $\delta\Delta G_i < \Delta G^*$ the ions can cross the smaller barrier for INU, recombine and then continue to grow as a neutral particle. However since r^* is always greater than r^u it can happen that the ion is neutralised before r^* has been passed, thus resulting in the evaporation of the aerosol. Therefore a correction is needed for Eq. (4). One suggested correction is a probability factor P_i ([Hamill et al., 1982](#))

$$P_i(\tau) = e^{-\sqrt{Q\alpha}\tau} \quad (5)$$

where $\sqrt{Q\alpha}$ is the inverse of the lifetime of an ion due to recombination, Q is the ion production rate, α the recombination coefficient, and τ is the required time for an ion to grow to the size r^u . Based on this equation the authors conclude that INU is negligible in the stratosphere but that nucleation onto stable ion-ion recombination clusters can enhance stratospheric nucleation as suggested by [Arnold \(1980\)](#). [Raes and Janssens](#)

(1985) argued against this solution and suggested an alternative where the ions were divided into two species: $N_{i,1}$ which are the ions below r^u centered at r^s and $N_{i,2}$ which are the ions between r^u and r^* :

$$J_{i,a} = BP'(\tau') + \frac{KN_{i,2}^2}{2} \quad (6)$$

5 where B is the right hand side of Eq. (4) except $N_{i,1}$ is substituted for N_i and $P'(\tau')$ is the chance that an $N_{i,2}$ ion is not lost by recombination with another ion nor is scavenged within the time needed to grow from r^u to r^* . The last part of Eq. (6) corresponds to the recombination of two $N_{i,2}$ ions (K is the recombination coefficient) which in most cases will result in a cluster larger than r^* . Using this solution it was shown that for the
10 sulphuric acid-water system there exists an interval of sulphuric acid concentrations where INU will dominate – this interval is below the lower limit of where homogeneous nucleation can take place. At 25°C and 75% relative humidity this interval goes from about 10^7 to $5 \cdot 10^8$ molecules of sulphuric acid per cubic centimeter. That INU can occur in conditions where homogeneous nucleation cannot is also indicated by Kiang
15 and Stauffer (1973).

A more elaborate model was developed by Laakso et al. (2002). Here ion nucleation was described in a way similar to the classical approach producing stable clusters at a given size, but the following growth by condensation and coagulation was described in detail. Particle sizes go from 0.5 to 1000 nm radius divided into 37 bins, 10 of which
20 are below 1 nm and the remaining increase logarithmically in size from 1 nm and up. The particles below 10 nm were divided into three charge categories: +1, 0 and –1 charge whereas the larger particles could have up to five charges of either sign. A special category for ions smaller than 0.5 nm was also included. In order to investigate the possibility that nucleation occurs only on negative ions the model was tested with
25 positive nucleation disabled. Similar amounts of particles were observed as when both positive and negative nucleation was allowed due to more sulphuric acid being

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available and because charged particles were not lost due to recombination with each other but only recombined with smaller ions of the opposite sign. Runs of the model at various temperatures and relative humidities showed that some nucleation events (Hörrak et al., 1998b; Mäkelä et al., 1997) could be explained quite well by the model while others (O'Dowd et al., 1999; Dal Maso et al., 2002) could not.

3.2 Kinetic theory

The advent of modern computers has allowed for a kinetic treatment of nucleation in which every reaction involved can be solved numerically. This method provides detailed descriptions of the size distribution of clusters starting with the gas phase monomers as opposed to the thermodynamic approach where the process leading to nucleation is not considered. For a given cluster three basic things can happen: 1) growth by the condensation of a gas phase monomer unto the cluster; 2) loss of mass by the evaporation of a monomer from the cluster; and 3) growth by coagulation with another cluster. When ions are present charged and neutral species can be treated separately. The standard General Dynamic Equation describing the evolution of neutral clusters can be seen in the book by Seinfeld and Pandis (1998, Chap. 12).

One of the first kinetic models was developed by Yu and Turco (1998) in order to simulate exhaust plumes from aeroplanes. First, processes were so fast that the thermodynamic solution did not apply and second, the evolution of heat in the plumes resulted in very high ion concentrations. Coagulation, condensation and evaporation were treated, and neutral, positive and negative clusters were examined from 0.56 nm to 5 μm with individual bins for the first 5 molecules and bin sizes increasing by 20% per bin hereafter. All the parameters used were calculated from theory. The model was adapted to investigate the role of ions, referred to by the authors as Ion Mediated Nucleation, on the atmosphere in general (Yu and Turco, 2001) using the water and sulphuric acid binary nucleation scheme. Specifically it was used to simulate one of the hitherto unexplained nucleation events reported by Clarke et al. (1998) and did so with succes. The sensitivity of aerosol formation to the ion production rate was likewise

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investigated, and it was concluded that the effect of changing ion production is highest when the ion production and the pre-existing aerosol surface are low to begin with and when condensable gas concentrations are high. Furthermore the model was used to study ion mobility spectra by Hörrak et al. (1998b) and a nucleation event from Idaho Hill, Colorado (Weber et al., 1997), and both cases were simulated with reasonable success (Yu and Turco, 2000). The main conclusion from the model was that INU is most likely to occur in and above the marine boundary layer.

Lovejoy et al. (2004) took the modelling one step further by including experimental measurements of the early steps of ion clustering to overcome the problems theory encounters with small size clusters. Thermodynamics for the attachment of water and sulphuric acid to $\text{HSO}_4^- (\text{H}_2\text{SO}_4)_x (\text{H}_2\text{O})_y$ for $x \leq 6$ and $y \leq 10$ and to $\text{H}^+ (\text{H}_2\text{SO}_4)_x (\text{H}_2\text{O})_y$ for $x \leq 4$ and $y \leq 15$ were measured (Froyd and Lovejoy, 2003a,b) to provide input to the model – for larger clusters the measurements converged to the theoretical results. For the neutral clusters theory was applied with a correction to obtain nucleation rates similar to those from Ball et al. (1999). Positive ions were treated as a single species since negative ions seem to be the most active. Negative ions and neutrals were divided into 60 bins up to a size of $1 \mu\text{m}$. Model runs were compared with a suite of observations and were in agreement with measurements done when $T < 270 \text{ K}$ – they underpredicted nucleation rates at higher temperatures and it was concluded that INU with the sulphuric acid and water system explains nucleations in the remote middle troposphere but generally not in the boundary layer, a conclusion that is contrary to that of Yu and Turco (2001). The results of the model were also described by Curtius et al. (2006). In 2006 Yu (2006a) presented the second generation of the Yu and Turco model (Yu and Turco, 1998) using improved theory for the description of small charged clusters and a new scheme for evaporation taking into account thermodynamic data. The original conclusion that INU of sulphuric acid and water can play a significant part in the lower atmosphere, including the boundary layer, was re-confirmed. Differences between this model and the one by Lovejoy et al. (2004) were mentioned and the model details were further discussed in the corresponding discussion paper (Yu, 2006b). The

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model (Yu, 2006a) was later incorporated into the GEOS-Chem global chemical transport model, producing a global map of calculated nucleation rates by INU. This was compared with an updated list of land based nucleation events based on the review by Kulmala et al. (2004b) along with nucleation rates reported by ship and aircraft measurements. It was found that most of the observations agreed with the predictions by the model with a few notable exceptions where other mechanisms such as nucleation of iodine species are thought to have dominated.

Molecular reactions can also be approached by ab initio calculations. Structures of $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_x$ (Curtius et al., 2001) and $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_x(\text{H}_2\text{O})_y$ (Froyd and Lovejoy, 2003a) have been done at the Hartree-Fock level while calculations on the hydration of HSO_4^- and H_2SO_4 have been performed by Kurtén et al. (2007) using high level Møller-Plesset perturbation theory.

3.3 Other theories

Tinsley (2000) suggested that the effect of cosmic rays on the global electrical circuit may in turn influence the microphysical processes in clouds, specifically the nucleation of ice particles. Changes in cosmic ray intensity alter the conductivity of the atmosphere and therefore the fair weather current J_z . Near the edges of clouds a space charge is created that allows aerosols to build up a large amount of like charge without suffering neutralisation. Evaporation of water from these particles results in highly charged particles with a coating of condensable gases. The enhanced charge on the particles allows for rapid coagulation (electro-scavenging) with larger droplets and due to the coating of the charged particles this can result in ice nucleation, changing the properties of the clouds. If J_z can influence cloud properties, other effects altering J_z would also play a part and this was also investigated in the study. A more thorough review of this mechanism has been made by Gray et al. (2005).

It was recently proposed that the formation of sulphuric acid could take place in clusters containing ozone, SO_2 and water without UV light (Svensmark et al., 2007; Sorokin and Arnold, 2007). In the mechanism proposed by Svensmark et al. molecular

oxygen picks up a negative charge, takes up water to form a cluster and then switches with ozone to form $\text{O}_3^-(\text{H}_2\text{O})_n$ (Fehsenfeld and Ferguson, 1974). SO_2 is then taken up by the cluster and oxidised:



5 Alternatively the oxidation could occur outside of a cluster with subsequent hydration:



Formation of sulphuric acid can then occur inside the cluster:



10 Following this the electron in the cluster could be ejected, e.g. due to the release of chemical energy within the cluster and thus become available to repeat the process. This implies that nucleation by the way of ions is not limited by the ion production rate. Instead the limiting factor is the rate of cluster production relative to the loss rate of ions by recombination and scavenging by larger clusters: the number of times a single ion can produce a stable cluster. The mechanism could also proceed by a variety of other
15 pathways – several options are listed by Sorokin and Arnold (2007).

3.3.1 Sign-preference

The apparent preference of anions for nucleation reported in several studies (Laakso et al., 2004a, 2007; Iida et al., 2006; Wilhelm et al., 2004) has been investigated theoretically. Using a molecule-based approach called Dynamical Nucleation Theory it
20 was concluded that not only the sign of the core ion but also its size plays a part: for instance water prefers a small cation over a large anion (Kathmann et al., 2005). Quantum chemical ab initio calculations applied to the problem showed that the electronic structure of the core ion and its interaction with the intermolecular bonds formed during nucleation determines the effect the core ion has on the cluster formation process.

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Thus using the sign and size of the ion alone is insufficient to determine its effectiveness as a core ion (Nadykto et al., 2006). These results were further discussed by Kathmann et al. (2007) and Nadykto et al. (2007). At present no calculations on sulphur species are available for comparison which would be interesting from an atmospheric point of view.

3.3.2 Charged fraction

In several observations (Vana et al., 2006; Iida et al., 2006; Laakso et al., 2007; Kompula et al., 2007) the charged fraction of the particles are used to evaluate the contribution of INU. Since particles nucleate below the limit of detection the charged fraction may change from the time of nucleation and until detection. Kerminen et al. (2007) described how the charged fraction of a particle population evolves with growth and found that it is dependent on two factors: the cluster ion concentration and the growth rate of the population (corresponding to the amount of condensable gases) such that at high ion concentrations and/or low growth rates the information on the original charging state may be lost when the particles are detected. If the electron can be ejected from a cluster due to the release of chemical energy as suggested by Svensmark et al. (2007) the charged fraction would also be reduced. Thus care must be taken when using the charged fraction as a tool for analysis.

4 Experiments

In order to test the theories and understand what to look for in field studies it is necessary to do experiments under controlled conditions. There are two main approaches to experimental investigation of INU. One approach operates on a macroscopic level trying to determine the influence of ions on bulk nucleation. The second approach is to investigate the molecular reactions taking place in an attempt to understand each step in the mechanism of particle formation.

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4.1 Bulk nucleation

The first of this kind of experiments are the ones conducted by [Wilson \(1895, 1899\)](#) where an expansion chamber was exposed to various kinds of ionising radiation, and an increase in density of the resulting fog was reported. With the advent of particle counters more detailed studies became possible, and the relation between generated particles and radiation doses of alpha rays from ^{220}Rn , beta rays, and x-rays were reported ([Megaw and Wiffen, 1961](#)) using a Pollak condensation nucleus counter ([Metnieks and Pollak, 1959](#)). The doses used were from ~ 1 to 15 rads forming ion concentrations orders of magnitude above atmospheric levels, and using this span of doses the particle production rate was increased by more than a factor of 100. A correlation of particle number with SO_2 was also reported. [Bricard et al. \(1968\)](#) reported a similar effect in an experiment where the charged fraction of the detectable particles (> 100 nm) was measured by applying an electrical charge to a metal tube placed prior to the particle counter, thus removing charged particles. It was shown that a measurable charged fraction only appeared about 50 min after the injection of ^{220}Rn . However the limit of particle detection (100 nm) was so far above the size at which nucleation happens that the experiment did not reveal much about the mechanism of nucleation.

Later experiments investigated whether ionisation could convert SO_2 into sulphate and thus particles. Radon was introduced into a system of air, SO_2 , O_3 and C_2H_4 resulting in four times as many particles as previously ([Vohra et al., 1984](#)). Realistic Radon levels (100 pCi m^{-3}) but very high SO_2 concentrations (300 ppb) were used. This was investigated further ([Raes et al., 1985](#)) in a study where a mixture of SO_2 (500 ppb) and NO_2 (15 ppb) were exposed to UV, UV + γ -rays and γ -rays alone. It was concluded that at the higher dose rates (3.4 to $32 \mu\text{Gy s}^{-1}$) the γ -rays produced sulphuric acid directly while at lower dose rates INU may have taken place. This means that using extreme radiation levels may cause false positive results since the amounts of sulphuric acid produced directly by radiation will be insignificant at natural radiation levels.

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An increase of nucleation rate was likewise observed for carbon tetrachloride, chloroform, o-xylene, methanol, ethanol and water in a thermal diffusion cloud chamber exposed to α -radiation (Rabeony and Mirabel, 1987). Using an electric field to ensure that only ions of one sign were present in the nucleation zone a preference for negative ions was observed, as well as a strong dependence on the strength of the applied electrical field such that the nucleation rate decreased with increasing field strength. By dividing the chamber into two sections and doing the charge separation and nucleation in separate sections it was possible to investigate the sign-effect with no electrical field present, and it was shown that in this case positive and negative ions increased nucleation by equal amounts. In an older study (Loeb et al., 1938) experiments with substances showing negative, positive and no sign preference were described. That the sign preference is dependent upon the species present is well in line with the theoretical work previously mentioned (Nadykto et al., 2006).

Another nucleation experiment was performed by Kim et al. (1997). Nucleation of an $\text{SO}_2/\text{H}_2\text{O}/\text{N}_2$ mixture was initiated by exposure to an ^{241}Am α -source producing both ions and OH-radicals. The charged fraction of particles was measured with a CPC (TSI model 3025) by applying a voltage to the collector leading to the CPC thus removing charged particles. With no added SO_2 the charged fraction was found to be 1, indicating INU and as SO_2 was added the charged fraction decreased as homogeneous nucleation started to play a part. For this system a negative sign-preference was found by two methods. Firstly the charged fractions were examined and secondly the electrical mobility distributions for positive and negative particles revealed a stronger activation by negative ions. In later work by the same group (Kim et al., 1998) the presence of NH_3 was found to enhance particle formation and decrease the charged fraction.

Some interesting nucleation results have been obtained by Berndt et al. (2005, 2006). Using a flow tube they observed nucleation in the sulphuric acid/water system. OH-concentrations were inferred from observed loss-rates of otherwise non-interfering organic species and then used to calculate the sulphuric acid concentration. When the

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5 sulphuric acid was generated by evaporation from a liquid reservoir the limit for nucleation was above 10^{10} cm^{-3} which is in line with observations by other investigators (Ball et al., 1999; Wyslouzil et al., 1991; Viisanen et al., 1997). However when the sulphuric acid was generated in situ by photolysis of ozone and subsequent oxidation of SO_2 the limit was found to be around 10^7 cm^{-3} which corresponds to atmospheric levels (Kazil et al., 2006). No explanation for this low limit for nucleation was given, but INU as well as ternary nucleation was ruled out, the former due to the lack of a significant charged particle fraction. Sorokin and Arnold (2007) argued, by considering the time required for aerosol growth in the flow tube, that the sulphuric acid concentration must have been larger in the experiment (around $7 \cdot 10^8 \text{ cm}^{-3}$).

10 An experiment in a 7 m^3 reaction chamber (Svensmark et al., 2007) showed a linear correlation between nucleated particles and ions for the $\text{H}_2\text{O}-\text{H}_2\text{SO}_4$ system. Where sulphuric acid was produced by photolysis at atmospheric levels of SO_2 (≤ 230 ppb), O_3 (~ 25 ppb) and ionisation ($1000-6000 \text{ ions cm}^{-3}$) with $[\text{H}_2\text{SO}_4] \sim 10^7-10^8 \text{ cm}^{-3}$, showing that INU can happen under atmospheric conditions. By applying an electrical field that reduced the lifetime of a small ion to less than a second the particle production was decreased by up to 50%, suggesting that INU occurs via a process that is fast compared to the recombination time of an ion (~ 200 s at ground level).

4.2 Molecular reactions

20 By investigating directly the molecules involved in the nucleation process more information about details of the mechanism may be revealed. Castleman Jr. (1982) used a mass spectrometer to investigate the clustering of water, CO_2 and SO_2 with a large assortment of core ions. Enthalpies, entropies and equilibrium constants were reported. Froyd and Lovejoy investigated the attachment of water to $\text{H}^+(\text{H}_2\text{SO}_4)_s(\text{H}_2\text{O})_w$ (Froyd and Lovejoy, 2003b) and to $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_s(\text{H}_2\text{O})_w$ (Froyd and Lovejoy, 2003a) using mass spectrometry, and the thermodynamics of sulphuric acid ligand bonding to these clusters were calculated. By showing the existence of a thermodynamic barrier for the

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addition of sulphuric acid to the positive cluster it was concluded that the negative pathway is favoured for the sulphuric acid-water system. The pressure and temperature dependence of the thermal decomposition of $\text{HSO}_4^-(\text{HNO}_3)_y$ and $\text{HSO}_4^-\text{H}_2\text{SO}_4\text{HNO}_3$ was measured in an ion trap (Curtius et al., 2001). These results were used to verify a master equation for thermal decomposition (Lovejoy and Curtius, 2001).

The evolution of clusters in the sulphuric acid-water system was observed by Wilhelm et al. (2004) in a large ion mass spectrometer. Cluster ions $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_a(\text{H}_2\text{O})_w$ and $\text{H}^+(\text{H}_2\text{SO}_4)_a(\text{H}_2\text{O})_w$ were grown with sulphuric acid. It was found that the mole fraction of sulphuric acid approached that of neutral clusters with increasing cluster size. Small negative clusters had more sulphuric acid than neutrals and the small positive clusters had less. The clusters did not grow to the sizes expected from the rate of collision between clusters and sulphuric acid, meaning that detachment of sulphuric acid played an important role. It was also shown that growth was more effective for negative than for positive clusters. A later study using the same setup (Sorokin et al., 2006) determined the hydration constants for the clusters and using the obtained data together with data from Froyd and Lovejoy (2003a) the authors simulated the obtained mass spectra.

5 Summary

Evidence for the importance of ions in aerosol nucleation is accumulating. Atmospheric observations indicate that binary homogeneous nucleation cannot explain some significant nucleation events, and ions may be the key. The fact that the exact mechanism for the nucleation is not known makes it difficult to obtain reliable observations since it is uncertain which parameters should be observed. It has also been a problem that the available technology has not been able to detect nucleating particles, something that could be greatly facilitated by the new instrument described by Kulmala et al. (2007).

As more and more data becomes available the theories also improve. However, modellers investigating the evolution of charged clusters in the sulphuric acid-water system still do not agree where in the atmosphere INU can take place. Also alternate



pathways for the nucleation process are still being explored – one possibility is that one ion can nucleate several aerosols.

It has been proven experimentally that ions can enhance nucleation under a variety of conditions including atmospheric. However, more investigations under atmospheric conditions are required to confirm and quantify the effect at varying temperatures and pressures. To further elucidate the potential impact on cloud formation, growth from freshly nucleated particles to cloud droplets must be investigated.

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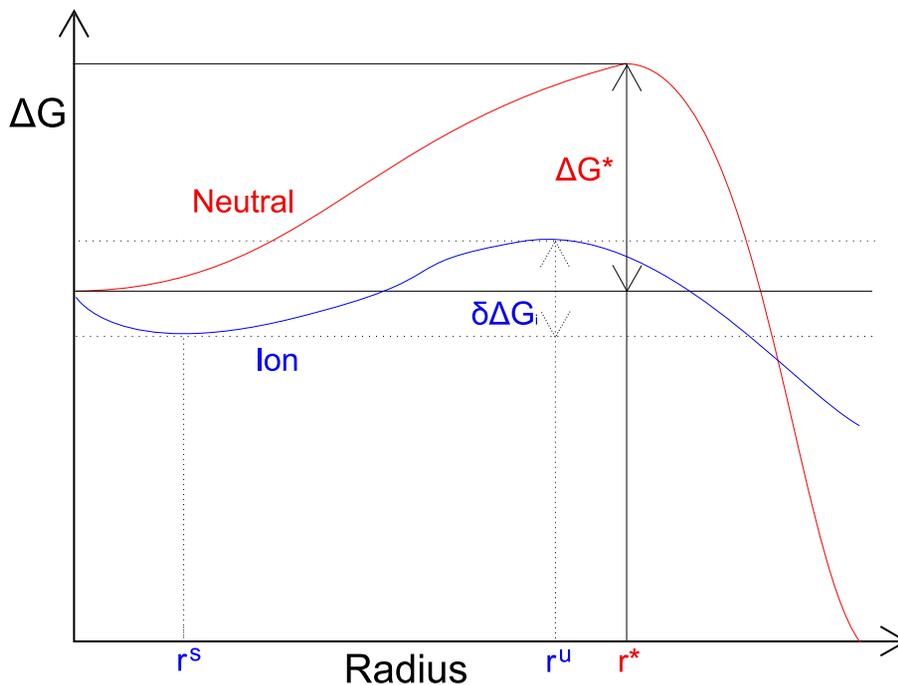
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Fig. 1. Energy barriers: The red line depicts the Gibbs free energy of a neutral cluster as a function of size. The blue line corresponds to a cluster containing an ion. Adapted from Curtius et al. (2006).

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