Nucleation/Nucléation

Nucleation of atmospheric aerosol particles

Joachim Curtius

Institute for Atmospheric Physics, University of Mainz, 55128 Mainz, Germany

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Abstract

A significant fraction of the total number of particles present in the atmosphere is formed originally by nucleation from the gas phase. Binary nucleation of sulphuric acid and water, ternary nucleation of sulphuric acid, water and ammonia and ion-induced nucleation are thought to be the most important aerosol nucleation processes in the atmosphere. Within the last two decades, instrumentation to observe and characterize nucleation has improved greatly and numerous observations of nucleation have been made including quantification of the nucleation rate, characterization of the growth process and first chemical characterizations of the freshly formed particles. Nucleation has been observed at many different places in the atmosphere: in the boundary layer, in the free troposphere, in remote locations, in coastal areas, in boreal forests as well as urban areas and pollution plumes. In most cases gaseous sulphuric acid is assumed to be the key precursor gas. After nucleation, other supersaturated substances, especially low vapour pressure organics often take part in the subsequent aerosol growth. Iodine oxides seem to be responsible for nucleation observed in some coastal areas.

Recent advances in modelling allow for a kinetic treatment of the nucleation process based on measured thermochemical data for the cluster formation. Considerable improvement over the classical nucleation treatment is expected from this approach.

A detailed understanding of atmospheric aerosol nucleation processes is needed as the freshly formed particles directly influence the number concentration and size distribution of the atmospheric aerosol. The formation of clouds and precipitation is affected and influences on climate are anticipated. Anthropogenic emissions influence atmospheric aerosol nucleation processes considerably.

Despite the comprehensive research efforts, substantial inconsistencies remain and conflicting results of laboratory studies, model studies as well as atmospheric observations persist. Several key questions about the predictability of atmospheric nucleation in general, about the substances, that take part in nucleation and subsequent growth and about the size and composition of the critical cluster, have not been resolved so far. ***To cite this article: J. Curtius, C. R. Physique 7 (2006).***
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Résumé

Nucléation de nouvelles particules dans l'atmosphère. Une fraction significative du nombre total de particules présentes dans l'atmosphère est formée initialement par nucléation homogène à partir de la phase gazeuse. La nucléation binaire de l'acide sulfurique et de l'eau, la nucléation ternaire de l'acide sulfurique, de l'eau et de l'ammoniac, enfin la nucléation induite par les ions, sont vraisemblablement les processus de nucléation les plus importants dans le contexte des aérosols atmosphériques. Au cours des vingt dernières années, l'amélioration considérable des instruments de mesure a permis de nombreuses observations et caractérisations de la nucléation y compris la quantification du taux de nucléation, la caractérisation de la croissance et les premières caractérisations des nanoparticules dès leur formation. La nucléation a été observée en différents points de l'atmosphère : dans la couche limite, dans la troposphère libre, dans des zones éloignées de toute pollution, dans les zones côtières, dans les forêts boréales comme dans les zones urbaines et leurs panaches de pollution. Dans la plupart des cas, il est suggéré que l'acide sulfurique gazeux est le gaz précurseur essentiel. Après la nucléation, d'autres substances, notamment des composés organiques à basse pression de

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E-mail address: curtius@uni-mainz.de (J. Curtius).

vapeur saturante, jouent souvent un rôle dans la croissance des aérosols. Les oxydes d'iode semblent responsables de la nucléation observée dans certaines zones côtières. De récents progrès théoriques permettent désormais un traitement cinétique du processus de nucléation, basé sur les caractéristiques thermochimiques mesurées de la formation des agrégats moléculaires. Cette approche représente une amélioration considérable par rapport au traitement classique de la nucléation.

Il est nécessaire de comprendre en détail les mécanismes de nucléation des aérosols atmosphériques, car les particules fraîchement formées influent directement sur la concentration et la distribution en tailles des aérosols atmosphériques. La formation des nuages et les précipitations en sont affectées, influençant le climat. Les émissions anthropiques influent fortement sur les processus de nucléation.

Malgré des efforts de recherche de grande envergure, il reste des incohérences substantielles, les études de laboratoire restant en désaccord avec les modélisations comme avec les observations sur le terrain. Quelques questions cruciales restent à résoudre en ce qui concerne la possibilité de prédire la nucléation atmosphérique de façon générale, en ce qui concerne les substances jouant un rôle dans la nucléation, puis dans la croissance, et en ce qui concerne la taille et la composition de l'agrégat critique. ***Pour citer cet article : J. Curtius, C. R. Physique 7 (2006).***

1. Introduction

1.1. General

Aerosol particles are ubiquitous in the Earth's atmosphere. These particles influence climate, cloud formation, weather, visibility, atmospheric chemistry as well as human health. All liquid or solid particles suspended in air are defined as aerosol particles. Soot, pollen, sea salt particles, mineral dust, asbestos fibres, fly ash and many other types of particles are summarized by this definition [1,2]. Atmospheric aerosol particles extend over a very large range of sizes: from sub-nanometer sized clusters of molecules up to millimetre-sized dust particles. Particles are usually classified in four size ranges: nucleation mode (1–20 nm), Aitken mode (20–0 nm), accumulation mode (90–1000 nm) and coarse mode (>1 μm) [3]. The range of particle number concentrations observed in the atmosphere is also considerable: number concentrations of less than 10 particles cm^{-3} are found in the stratosphere at 20 km altitude [4], several thousand particles per cubic centimetre are typically observed in modestly polluted continental areas near the ground [5], more than 1×10^5 particles cm^{-3} are often observed in urban areas [5]. Somewhat surprisingly, also at sites considered remote and relatively free of pollution, like the west coast of Ireland, large particle concentrations of more than 1×10^6 cm^{-3} have been observed [6]. The vast majority of the atmospheric particles are smaller than 1 μm (sub-micron or fine particles) but the few coarse particles larger than 1 μm in diameter often make up a large fraction of the total aerosol mass.

Two groups of aerosol particles are distinguished: primary particles are those that have direct sources. Mineral dust particles dispersed from the ground, soot particles from combustion sources, sea salt particles from ocean spray, pollen and spores from biological sources fall into this category. Secondary particles are produced in the atmosphere by gas-to-particle conversion. Sulphates and nitrates and a suite of organic substances that make up the largest fraction of the sub-micrometre-sized aerosol particles belong to this category [1].

The atmosphere is divided in several layers, the lowest being the troposphere where temperature generally decreases with altitude. The troposphere is subdivided into the boundary layer and the free troposphere. The boundary layer constitutes the lowest ∼0.5–2 km where air mass characteristics such as wind direction, wind velocity, temperature and trace gas concentrations are strongly influenced by the presence of the Earth's surface, e.g. high concentrations of trace gases that are emitted at ground. The free troposphere is the region where the direct influences from the surface on wind velocity etc. are small. Between the boundary layer and the free troposphere a temperature inversion layer often limits the vertical exchange of air masses.

1.2. Relevance

Particles in the atmosphere scatter and absorb solar as well as terrestrial radiation. Therefore they influence the global radiation budget directly. Anthropogenic influences on the atmospheric aerosol burden are considered to influ-

ence global climate substantially [7,8]. Besides their direct effect on the radiation budget [9,10], a large fraction of the atmospheric aerosol particles acts as cloud condensation nuclei (CCN). When clouds form in the atmosphere, water condenses on the available cloud condensation nuclei. A changing number concentration of CCN modifies the number concentration and the size of the cloud droplets. Therefore the optical properties and the lifetime of atmospheric clouds change. This influence of particles on the global radiation budget and climate is termed the indirect aerosol effect [11]. Quantification of the effects of aerosol of anthropogenic origin on climate is still limited and the level of scientific understanding of these effects lacks detailed knowledge [8,12]. Here atmospheric nucleation processes may be especially relevant because the freshly formed particles can grow into sizes where they act as CCN and therefore influence cloud properties and climate [13–15].

Besides their impact on climate, atmospheric aerosol particles cause adverse health effects [16]. Especially ultrafine particles <100 nm in diameter that are inhaled are efficiently deposited in the alveoli of the lungs. Long-term exposure to fine and ultrafine particulate air pollution, common to many metropolitan areas, increases, for example, the risk of cardiopulmonary mortality and lung cancer mortality [17–19]. Many factors influence these health effects in detail, e.g. the size of the particles, their surface and morphology, their solubility and the toxicity of the chemical substances contained in the particles.

1.3. Nucleation

Pure sulphuric acid (H_2SO_4) has a low vapour pressure at atmospheric temperatures [20]. The H_2SO_4 vapour pressure is reduced further in the presence of water [21] due to the large mixing enthalpy that is freed when the two substances are mixed. When H_2SO_4 is produced from sulphur dioxide (SO_2) in the gas phase, it is therefore easily super-saturated and the gaseous H_2SO_4 starts to condense. Water vapour is omnipresent in the atmosphere and therefore a co-condensation of H_2SO_4 and H_2O is always occurring. If the gaseous H_2SO_4 molecules do not encounter pre-existing (aerosol) surfaces to condense on before colliding with other H_2SO_4 and H_2O molecules, they may cluster with the other molecules. If these clusters continue to grow and overcome the nucleation barrier (see below), then new, thermodynamically stable aerosol particles are formed from the gas phase. This is termed binary homogeneous nucleation: binary for the two substances H_2SO_4 and H_2O that nucleate and homogeneous because no other catalyst like a foreign surface is involved in the formation.

The formation of new aerosol particles from gaseous precursors has been observed at numerous locations in the Earth's atmosphere. Nucleation was observed in a variety of conditions and regions such as the free troposphere [22–27], forested [28–32] and coastal [33,34] areas, cities [35,36] and pollution plumes [37–39]. Kulmala et al. [3] reviewed more than 100 investigations on aerosol nucleation in the atmosphere. Nucleation was observed at a range of atmospheric and meteorological conditions. Many open questions remain about the details of the nucleation mechanism and about the nucleating agents. Up to now it can generally not be predicted when and where nucleation will take place. Nevertheless, the nucleation and subsequent growth processes influence the total particle number, the particle size distribution as well as the chemical and optical properties of the atmospheric aerosol. Climatic effects, like the indirect aerosol effects, are potentially influenced by the number of nucleation mode particles growing to sizes at which they can become active cloud condensation nuclei [15,40]. Sulphur dioxide is considered the most important precursor gas for atmospheric nucleation particles. It is emitted into the atmosphere mostly by anthropogenic sources such as combustion of sulphur-containing fossil fuels [41]. Therefore, aerosol nucleation in the atmosphere would be expected to be enhanced by anthropogenic activities. On the other hand, the pre-existing aerosol that can take up gaseous sulphuric acid and thereby suppress nucleation is increased as well by anthropogenic sources. Investigations on the overall anthropogenic influences on atmospheric aerosol nucleation are currently just emerging [15].

Several nucleation mechanisms have been discussed to occur in the atmosphere. The binary nucleation of sulphuric acid and water [42–45], the ternary nucleation of H_2SO_4, H_2O, and ammonia (NH_3) [46–49], and ion-induced nucleation [50–55] are most prominent.

Interestingly, out of the hundreds of different trace compounds in the atmosphere, only very few are able to nucleate new particles. Sulphuric acid, in combination with water vapour and ammonia, iodine oxides and some organic substances such as certain sesquiterpene oxidation products are currently the only substances known to produce significant amounts of new particles in the ambient atmosphere.

It is the scope of this article to give an overview of the field of atmospheric nucleation research and to provide the interested reader with references for more detailed up-to-date information. I will focus on the formation of new

secondary particles in the atmosphere by homogeneous aerosol nucleation. I will address briefly the theoretical fundaments of aerosol nucleation processes. Then some of the instrumentation to investigate atmospheric nucleation processes is described and an overview of the most important chemical systems known to be involved in atmospheric nucleation processes is given.

Two other types of nucleation processes that are as well of importance for the atmosphere will not be discussed in detail in the present article: the first is the condensation of substances onto a different substance: so-called *heterogeneous nucleation*, e.g. the wetting of a solid (particle) surface by water condensation as it occurs during fog and cloud formation (e.g. [2]). The other nucleation process which is also highly important for several atmospheric processes is *ice nucleation*. When ice crystals originally form in clouds, some kind of nucleation process is involved as well. The primary production of ice crystals in clouds is either induced by ice nuclei (IN, heterogeneous ice nucleation) or at cold temperatures below about −37 °C by homogeneous freezing of super-cooled droplets. Both processes involve a nucleation step. Ice nuclei are foreign bodies that catalyse the freezing process. Several different heterogeneous freezing processes involving ice nuclei exist like contact freezing (a super-cooled droplet freezes when it comes into contact with an ice nucleus), deposition freezing (ice grows directly onto an ice nucleus by deposition from the gas phase), and immersion freezing (an ice nucleus immersed in a super-cooled droplet triggers the freezing). The concentration of ice nuclei influences the radiative properties of clouds, cloud electrification and the formation of precipitation. Understanding the role of ice nuclei in cloud processing is therefore of high importance for climate and weather modelling. Mineral dust particles are considered favourable ice nuclei but currently many open questions remain concerning the physical and chemical properties of ice nuclei. In the atmosphere typically only one out of 10^3 to 10^6 aerosol particles acts as an ice nucleus. The homogeneous freezing processes are subject of active research as well as considerable advancements of the theory of homogeneous freezing of solutes have been made recently [56]. Once ice has formed in one of the primary processes then the ice number concentration as well as the mass can increase by secondary ice production processes like splintering and riming. For a recent review on atmospheric ice nucleation processes see Cantrell and Heymsfield [57].

From the physicists standpoint it is highly interesting to study the aerosol nucleation process, as it essentially describes the transition from single gas-phase molecules to a bulk phase liquid or solid. The most crucial steps in this process are located just in the transition region where the thermodynamics of small clusters of molecules govern the behaviour. For the chemical systems which are of highest relevance for the atmosphere, the properties of these clusters such as their density and surface tension are different from the corresponding bulk phase properties. We are currently just beginning to access these clusters experimentally as well as through quantum-chemical calculations and to reveal their properties.

2. Nucleation theory

Classical nucleation theory to describe aerosol formation was first formulated about 80 years ago [58,59]. Numerous advances and modifications to nucleation theory have been made since but the classical nucleation theory still forms the basis for the thermodynamic interpretation of aerosol nucleation processes. The Gibbs free energy G is the thermodynamic potential of choice to study atmospheric nucleation processes as the natural variables pressure and temperature can easily be measured. With pressure and temperature fixed, a closed thermodynamic system will be in equilibrium when G is minimal. We consider a substance A with its vapour pressure p_A. Its equilibrium vapour pressure over a flat surface of liquid A is $p_{A\infty}$. If the substance is supersaturated in the gas phase ($p_A > p_{A\infty}$) and far away from any other surfaces on which the gas-phase molecules could condense on, the system is metastable and the vapour molecules would generally prefer to undergo a phase transition to the condensed phase as a lower value of G could be obtained due to the lower chemical potential of the bulk liquid. For a single substance the thermodynamics of the nucleation are given by [2]:

$$\Delta G = -\frac{4}{3}\pi R_p^3 \frac{kT}{v_l} \ln S + 4\pi R_p^2 \sigma \tag{1}$$

This equation gives the change of the free energy G as a function of the nucleating particle's radius R_p. Fig. 1 illustrates the equation. Here S is the saturation ratio, $S = p_A/p_{A\infty}$, k is the Boltzmann constant, T is the temperature, v_l is the volume occupied per molecule, and σ is the surface tension. As long as the system is supersaturated, S is larger than l and the first term of the right-hand side of the equation is negative. Generally, this is the driving force for
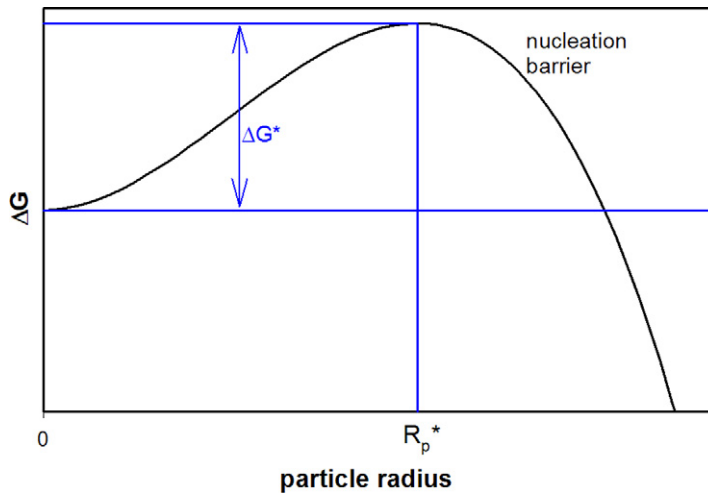
Fig. 1. Thermodynamic representation of aerosol nucleation. A nucleation barrier of height ΔG^* exists. The critical cluster size R_p^* is defined by the maximum of the barrier.

the gas-phase molecules to condense and thereby increase the particle radius. Just in the beginning, for small R_p, the second term plays an important role. As the particle forms, a new surface ($A_p = 4\pi R_p^2$) has to be build up, costing surface energy. In the beginning this surface energy is bigger than the energy won from changing from gas phase to particle phase and therefore for small R_p an effective energy barrier exists that prevents the gas from nucleation although it is supersaturated in the gas phase with respect to the flat surface equilibrium pressure.

The location of the maximum of the barrier marks the critical radius. Once a cluster has reached the size of the critical cluster, the droplet will persist and most likely grow by condensation of further gas phase molecules. For small clusters with sizes smaller than the critical size it is energetically more likely to evaporate off a molecule than another molecule condensing on them. In most cases such clusters will fall apart into separate gas molecules again. But there is a statistical chance that now and then a cluster collects so many molecules that it becomes large enough to reach the critical size and overcome the barrier.

From differentiation of (1) the height of the nucleation barrier ΔG^* and the position of the critical radius R_p^* can be determined:

$$\Delta G^* = \frac{4\pi}{3}\sigma R_p^{*2} = \frac{4\pi}{3}\sigma \left(\frac{2\sigma v_l}{kT \ln S}\right)^2 \tag{2}$$

This equation is known as the Kelvin equation. Just at the critical radius a particle has reached an instable equilibrium and will neither grow nor evaporate. Therefore the Kelvin equation connects also the equilibrium vapour pressure p_A^* of A over a spherical surface of radius R_p^* with the equilibrium vapour pressure over a flat surface $p_{A\infty}$.

The nucleation rate J is given as the number of clusters that grow beyond the critical size per second. The nucleation rate is connected to the height of the nucleation barrier by:

$$J = C \exp\left(-\frac{\Delta G^*}{kT}\right) \tag{3}$$

Here, C is a pre-exponential factor. There is a negative exponential dependence of the nucleation rate on the height of the nucleation barrier. The nucleation barrier determines the atmospheric nucleation processes. Pure water vapour, for example, will never undergo homogeneous nucleation in the atmosphere. When a cloud forms in the atmosphere at conditions slightly above 100% relative humidity, the water vapour molecules will always find a suitable pre-existing aerosol surface for condensation, i.e. a cloud condensation nucleus (CCN). Homogeneous nucleation of pure water alone at 20 °C and 200% relative humidity, a relative humidity far above any humidity ever observed in the ambient atmosphere, would still take 10^{54} seconds for one droplet to form in 1 cm^3, due to the high nucleation barrier for pure water at these conditions [2].

The fundamental nucleation theorem connects the number of molecules n_A^* of species A that form the critical cluster with the slope of the logarithm of the nucleation rate as a function of the logarithm of the saturation S of the nucleating species [60–62]:

$$\left[\frac{\partial \ln J}{\partial \ln S_A}\right]_T \approx n_A \tag{4}$$

The expression can be extended to binary systems [61]. It means, for example, that for binary nucleation of H_2SO_4 and H_2O the number of H_2SO_4 molecules in the critical cluster can be derived from measurements of the nucleation rate as a function of the H_2SO_4 concentration at fixed temperature and relative humidity [62,63].

The kinetic approach to describe the nucleation is based on setting up the appropriate rate equations. Let $N_i(t)$ be the number concentration of clusters containing i molecules, then the rate equation is given by:

$$\frac{\mathrm{d}N_i}{\mathrm{d}t} = k_{i-1}^f N_{i-1}(t) - k_i^r N_i(t) - k_i^f N_i(t) + k_{i+1}^r N_{i+1}(t) \tag{5}$$

The i-mer concentration is increased by condensation of an additional molecule on the $(i-1)$-cluster or by evaporation of a molecule from the $(i+1)$-cluster and it is decreased by condensation or evaporation of a molecule to or from the i-mer. The forward rate constants k^f and the reverse rate constants k^r characterize the efficiency of these reactions. Eq. (5) can be expanded, for example, by including coagulation of the clusters, loss to pre-existing aerosol particles and other surfaces.

So far we have discussed homogeneous systems consisting of one substance only. In the atmosphere often two, three or even more substances are involved in the nucleation process, as the equilibrium vapour pressures of mixed systems are generally lower than for the pure systems. The nucleation of sulphuric acid and water is the most important binary system for the atmosphere. The nucleation theory has been expanded to the binary system [43,44,64–66]. Here, the ΔG curve of Fig. 1 becomes a saddle-shaped surface, when ΔG is plotted as a function of the two components and the composition of the critical cluster is defined by the saddle point.

In the atmosphere the formation of new particles is often thought to be a two-step process: first the nucleation itself where clusters overcome the nucleation barrier and then the subsequent growth of these clusters. These two steps are often decoupled, as sulphuric acid/water clusters may nucleate to form thermodynamically stable clusters, but the gas phase sulphuric acid concentration is too small that these stable clusters could grow to observable sizes >2.5 nm before they coagulate with pre-existing particles [67]. Typical atmospheric gas-phase concentrations of sulphuric acid are $<5 \times 10^7$ molecules cm^{-3} and observed growth rates are too fast to be explained by uptake of H_2SO_4 and water alone. Here other condensable species, like supersaturated organics that are not supersaturated enough for their clusters to overcome the nucleation barrier themselves due to a large Kelvin effect, but that are much more abundant in the gas phase than sulphuric acid, will be responsible for most of the growth of the freshly nucleated particles. The schematics of such an atmospheric nucleation process of H_2SO_4 and H_2O with subsequent growth involving also organics is illustrated in Fig. 2. The particles eventually may grow large enough to act as cloud condensation nuclei.

In the atmosphere aerosol nucleation always competes with the uptake of condensable gases on the already existing aerosol particles. Nucleation will only occur, if the production of condensable species is faster than condensation on the pre-existent particles. The concept of the condensational sink (CS) has been established to characterize and model the losses of the condensing molecules on pre-existing particles [13].

Already C.T.R. Wilson discovered that nucleation around ions is a very efficient process to form new particles. His invention of the cloud chamber was used for the detection of ionising radiation in particle physics for decades [68]. First theoretical descriptions were given by J.J. Thomson [69]. The ion charge helps to stabilize the cluster as the electrostatic interaction prevents the cluster molecules from evaporating off the cluster as easily as in the neutral case. The nucleation barrier is therefore substantially lower in this case and the critical cluster is smaller. In the atmosphere, ions are produced continuously by galactic cosmic rays. Therefore, ion-induced nucleation might link cosmic radiation and global cloud cover [70].

The classical nucleation theory depends on several bulk phase properties such as the density, and the surface tension. When the bulk phase surface tension is used for the description, the term *capillary approximation* is frequently used. A cluster consisting of only a few molecules will most likely have properties much different from the bulk phase and it is difficult to determine the density and the surface area of such a cluster. Therefore the classical theory is limited and observed nucleation rates often differ by orders of magnitude from the ones predicted by classical theory (e.g.
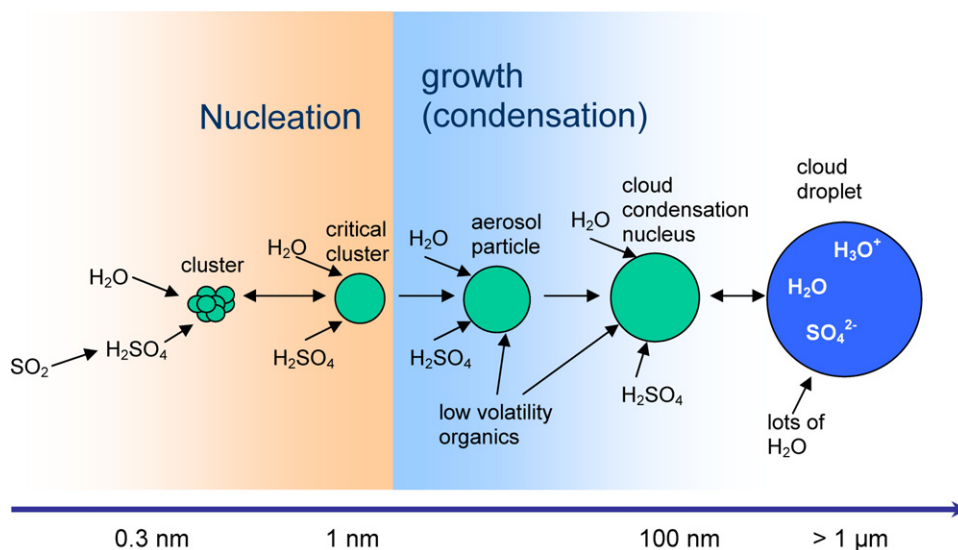
Fig. 2. Schematic representation of the nucleation and subsequent growth process for atmospheric binary homogeneous nucleation of H_2SO_4 and H_2O. Once stable clusters are formed, also other substances such as low-volatility organics can take part in the growth process. Particles may grow to sizes large enough to act as cloud condensation nuclei on which cloud droplets may form eventually.

[71]). Different approaches have been sought to overcome these shortcomings. As every condensation or evaporation of a molecule to or from a cluster corresponds to a chemical reaction, the formation process can be treated as a series of association and dissociation reactions. If all the standard changes in ΔG^o for each of these reactions are known molecule by molecule, the ΔG-curve or surface can be constructed avoiding the limitations of the classical theory for small clusters. Unfortunately, thermochemical data for the clusters of atmospheric interest is scarce. For the ion-induced nucleation process measurements and quantum-chemical calculations for clusters of sulphuric acid and water were performed to derive the changes of the thermochemical potentials [72–76]. Thereby the ion-induced nucleation pathway can be modelled based on experimentally derived thermochemical data [54]. For a more detailed introduction to ion-induced nucleation see Curtius et al. [77]. Recently, thermochemical data from laboratory measurements for the neutral hydrated sulphuric acid dimer and trimer have also been reported [45].

Parameterised equations of the nucleation rates, size of the critical cluster and critical cluster composition as a function of the gas-phase concentration of the involved chemical species and as a function of temperature have been derived for the binary H_2SO_4/H_2O system [43], the ternary $H_2SO_4/H_2O/NH_3$ system [78] as well as for the ion-induced nucleation of the H_2SO_4/H_2O system [79]. Recently, the predictions of nucleation from these three parameterisations have been compared in a global model [80].

A more comprehensive treatment of aerosol nucleation theory is beyond the scope of this article. For a broad introduction to the atmospheric nucleation theory see Seinfeld and Pandis [2], and the review article by Laaksonen et al. [81].

3. Instrumentation

To observe nucleation in the atmosphere it is necessary to detect the nucleation mode particles with diameters of 1–20 nm. Especially the evolution of the number concentration, the size distribution and the chemical composition of the nucleation mode particles are of interest. Of the various instrumental methods, a few of the most important ones will be addressed here. Powerful instrumentation that enabled the study of nucleation mode particles became available for atmospheric measurements during the past two decades. To count the total number concentration of all particles larger than a certain diameter, Condensation Nucleus Counters (CNC) are widely used. To measure the size distribution of ultrafine aerosol particles, nano-Differential Mobility Analysers (nDMA) are operated. Techniques to analyse the chemical composition of nucleation mode particles are still rare. A few techniques that have been developed recently will be discussed.

To interpret the nucleation measurements, also the concurrent measurement of the nucleating vapours and their precursor gases is needed. These measurements need to be highly sensitive as the nucleating vapours are usually present in the atmosphere at the pptv level (parts per trillion by volume, equals picomole per mole) or below. For example, gas-phase sulphuric acid is detected by Chemical Ionisation Mass Spectrometry with detection limits as low as 10^4–10^5 molecule cm^{-3} [82,83]. Quantitative sampling of the precursor gases is demanding due to wall losses of the low-volatility gases in the sampling lines.

3.1. Condensation Nucleus Counters

Atmospheric ultrafine particles (smaller than 100 nm) cannot be detected optically because light scattering is inefficient at these sizes. To count these particles it is therefore necessary to grow them first to optically observable sizes. Various types of Condensation Nucleus Counters (CN-Counters) have been developed for this purpose; see McMurry [84] for a review of the century-long history of CN-Counters. In these counters the aerosol sample flow is brought into contact with a supersaturated vapour, for example *n*-butyl alcohol (butanol) vapour. The supersaturation is well defined by maintaining a saturation equilibrium between liquid and gas-phase butanol at a higher temperature (saturator) and then guiding the saturated vapour into a cooler region (condenser) where the butanol rapidly condenses onto the particles. Thereby all particles larger than the respective Kelvin diameter ('cut-off' diameter) for the chosen butanol supersaturation (cf. Eq. (2)) will grow to sizes larger than 1 µm and can then be counted by suitable laser optics and photodiode detectors. By measuring the aerosol sample flow through the instrument the particle number concentration is calculated. The cut-off size of the CNC is determined by the supersaturation which is controlled by the vapour pressures of butanol at the chosen saturator and condenser temperatures. Larger particles are activated and will be counted, smaller particles will not grow because the saturation is not high enough for them to grow.

Diffusion losses inside the CNPC instruments and inhomogeneities of the supersaturation of the working fluid limit the smallest feasible cut-off diameters: particles in the 1–3 nm region are rapidly lost to the inner walls of the sampling lines by diffusion. Homogeneous nucleation of the working fluid limits the maximum temperature difference between the saturator and the condenser. Currently, commercially available CNPCs have cut-offs down to 2.5 nm (e.g. TSI Inc. CNPC Models 3776 and 3786). Nevertheless, for nucleation research it would be important to detect even smaller particles. The goal is to measure the true nucleation rates and not the apparent nucleation rates. Then, the growth process could be decoupled from the nucleation and there would be no time lag between the occurrence of nucleation and the actual atmospheric measurement. Today, CN-Counters operating in a continuous flow-mode are widely used and replaced the original non-continuous counters where an adiabatic expansion is used to create the super-saturation [84,85]. In adiabatic expansion CNPCs diffusion losses of the smallest particles can be minimized efficiently and recent developments of automated adiabatic-expansion counters may allow to detect particles also at sizes below 2.5 nm [86].

The presence of nucleation mode particles can be detected by using two CNCs with different cut-off diameters. Operating one CNPC with a 3 nm cut-off and another one with a 6 nm cut-off, from the difference of the two concentration measurements the number of particles in the 3 to 6 nm size range is measured (e.g. [24,38,53]). Similarly, pulse-height analysis of the CNC detector signal has been used to identify particles in the 3–10 nm size range [34,39,87]. In the atmosphere, such small particles must have formed by nucleation processes because particles from primary sources are always larger in size. Furthermore, the formation must have been recent because the nucleation mode particles grow by condensation and are lost by coagulation with larger particles and therefore a nucleation mode of particles <10 nm is rather short-lived in the atmosphere and consists typically only for a few hours to one day.

3.2. Nano-Differential Mobility Analysers

The aerosol size distribution can be monitored by use of a Differential Mobility Analyzer (DMA) [88]. Here the particles are separated according to their electrical mobility which can be connected to their diameter [89,90]. With the DMA, only charged aerosol particles are classified but because the size-dependent equilibrium particle charge distribution is known, the total aerosol size distribution including the uncharged particles can be calculated. Once the particles are separated according to their electrical mobility, the monodisperse particles can be counted using either a CNC or a Faraday cup aerosol electrometer. Nano-DMAs that minimize the diffusional losses have been constructed to measure charged particles down to sizes of 1 nm [91,92].

Using a set of CNPCs with different cut-offs instead of a nano-DMA to measure atmospheric nucleation processes is advantageous in certain situations, especially for aircraft-based measurements, because CNPCs achieve significantly higher sampling frequencies and much better detection limits than nano-DMAs.

3.3. Chemical characterization of nucleation mode particles

Chemical analysis of nucleation mode particles is extremely difficult due to the very small amounts of material available. Let us consider, for example, an atmospheric nucleation event producing 1000 particles cm^{-3} of 5 nm diameter. The concentration of these particles can easily be measured using a nano-DMA or a set of CNPCs (see above). However, the total mass amounts only to about 0.1 femtogram per cubic centimetre. In general, neither off-line analysis techniques like various chromatographic or electron microscopic techniques nor on-line techniques like aerosol mass spectrometry are able to analyse the chemical composition of such miniscule amounts. Additionally, the analysis has to assure that larger pre-existing particles as well as gaseous compounds are efficiently excluded. Only a few techniques have been demonstrated to be suitable for chemical analysis of atmospheric nucleation mode particles: the elemental composition of particles <10 nm determined by energy-dispersive X-ray transmission electron microscopy (EDX-TEM) revealed iodine in nucleation particles sampled at the coast of Ireland [93] and led to the discovery of iodine oxides as the most probable nucleating agents for the nucleation events observed at the coast of Ireland [94], see below. A promising new development for chemical composition measurements is the thermal desorption chemical ionisation mass spectrometer (TDCIMS) [95]. Here, for example, chemical composition measurements in the 6–15 nm size range revealed mostly sulphate and ammonium as the primary components of nucleation particles sampled in Atlanta, Georgia [96]. Another promising approach, the nano-aerosol mass spectrometer (NAMS) has been developed recently by Johnston and co-workers [97].

Several indirect methods have been employed to gain information on the chemical composition. For example, by studying the hygroscopicity of nano-particles more hygroscopic substances like sulphuric acid can be distinguished from less hygroscopic ones like iodine oxides or organics in the atmosphere [93]. O'Dowd et al. studied the details of the detector pulses from CN-Counters (pulse height analysis). From the shape of these pulses also chemical differentiation can be gained, e.g. nanometre sized particles of organic acids can be distinguished from sulphate particles [98,99].

4. Laboratory studies

In the laboratory numerous techniques have been used to study particle nucleation processes, including experiments with fast expansion chambers (e.g. [62]), flow reactors (e.g. [63,100]), and aerosol chambers (e.g. [101]). In particular, the atmospherically relevant nucleation of H_2SO_4 and H_2O has been studied various times [63,71,100, 102]. Nucleation studies of sulphuric acid and water are complicated because sulphuric acid is assumed to be lost at every collision with the reactor walls. The measurement of gaseous H_2SO_4 is challenging as well. Therefore, an exact quantification of the H_2SO_4 concentration in the nucleation zone is difficult.

As an example, two studies of the nucleation of H_2SO_4 and H_2O are discussed here: Ball et al. [63] measured the nucleation rate at 295 K including for the first time a direct measurement of the gaseous H_2SO_4 vapour. Here gas-phase H_2SO_4 was produced from a heated liquid H_2SO_4 reservoir. Nucleation rates >1 s^{-1} cm^{-3} occurred for $[H_2SO_4] > 6 \times 10^{10}$ molecule cm^{-3} in the nucleation zone at RH = 15%. The critical cluster was derived to consist of typically 7–8 molecules of H_2SO_4 and 5 molecules of H_2O. In this study H_2SO_4 was measured directly, but it has to be noted that the measured values are corrected by a factor of 22 (+200%, −67%) to account for the losses between the nucleation zone and the mass spectrometer measuring H_2SO_4.

Berndt et al. found substantial differences for the observed nucleation rates depending on the production process for the gaseous H_2SO_4 [100]. When producing it from liquid H_2SO_4, nucleation rates agreed roughly with previous experimental studies. When producing the H_2SO_4 from SO_2 in the gas phase, then nucleation rates of 0.3–0.4 s^{-1} cm^{-3} occurred already for calculated $[H_2SO_4] \approx 10^7$ cm^{-3} which is close to H_2SO_4 concentrations typically observed in the atmosphere. Here, gas-phase H_2SO_4 was not measured during the experiments.

Besides studying nucleation events directly, laboratory studies were conducted to measure the thermodynamic properties of the molecular clusters that take part in the nucleation process [45,72–76] These measurements form the

basis for model calculations of atmospheric aerosol nucleation that do not depend on the assumptions of classical nucleation theory any more [45,54].

5. Atmospheric observations

A typical nucleation event as frequently measured by a nano-DMA in the boreal forest at Hyytiälä, Finland, is shown in Fig. 3. Between the late morning and early afternoon several thousand particles are first detected in the smallest size bins. Within a few hours these particles grow to sizes of about 50 nm. It is apparent that new particles are formed until so many particles are present that the condensable vapours are taken up efficiently and no more new particles are nucleated. The measurement is conducted at a fixed station and the fact that the development of the particle size distribution can be observed for many hours, demonstrates that these nucleation events are very stationary, happening simultaneously on regional scales so that the advection of air masses by the wind hardly changes the observations. From the displayed 'nucleation banana' the average nucleation and growth rates can be derived by determination of the number of additional particles over the nucleation time interval and by inspecting the increase in size of the nucleation mode diameter with time, respectively [3]. Alternatively, a more sophisticated analysis of the nucleation and growth processes by inverse modelling yields nucleation and growth rates at high time resolution [103].

Nucleation was observed in the free troposphere [22–27], in arctic [104,105], forested [28–32] and coastal [33,34] areas, cities [35,36] and pollution plumes [37–39] and various other locations (e.g. [106,107]). Typical formation rates for particles >3 nm are in the range 0.01–10 cm^{-3} s^{-1}, in urban areas up to 100 cm^{-3} s^{-1} and in coastal areas as high as 10^4–10^5 cm^{-3} s^{-1}. The growth rates are usually in the range of 1–20 nm h^{-1}, but rates as high as 1000 nm h^{-1}, sustained for seconds to minutes in coastal areas and as low as 0.1 nm h^{-1} in clean arctic environments have been observed [3]. Studies of the seasonal variability show that the frequency of nucleation events is highest in spring for Hyytiälä [3], and highest during wintertime for measurements at the mountain ridge Jungfraujoch [107]. General statements on the role of temperature conditions for the occurrence of nucleation events are difficult. On the one hand, lower temperatures mean lower equilibrium vapour pressures and gaseous nucleating compounds are more readily supersaturated. On the other hand many emissions that influence nucleation or growth are elevated at warmer temperatures such as the terpene emissions by vegetation (see below).

Only very few substances are known to nucleate particles in the atmosphere. Which substances are likely candidates? They need to be low-volatility substances produced in the gas phase from some abundant high-volatility precursor gas in large enough quantities so that the produced nucleating agent is forming faster than depletion by condensation on pre-existing aerosol or other loss and dilution processes take place. Only for these substances the necessary supersaturation is reached and nucleation will take place. The gas-phase production usually involves either a photodissociation of the precursor substance itself or the reaction with substances like the hydroxyl radical or ozone that are produced in the atmosphere by photochemical processes. Therefore nucleation events are observed almost exclusively during daytime. Two night-time nucleation events have been described that were both associated with
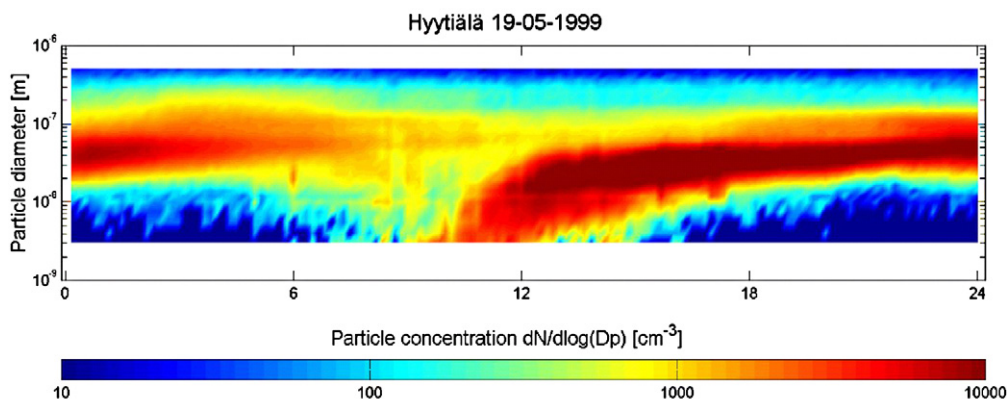

Fig. 3. Contour plot of the particle concentration as a function of time and particle size for a nucleation event observed in a boreal forest at Hyytiälä, Finland; 24 hours measurement for 19 May 1999. Between 9:00 and 12:30 numerous freshly nucleated particles appear at the smallest measurable sizes (>3 nm) and grow within hours to sizes of around 50 nm. From [149].

orographic clouds [108,109]. Nucleation processes to explain the night-time events not involving photochemistry are conceivable, e.g. the reaction of gaseous hydrochloric acid HCl with ammonia NH_3 forming low-volatility ammonium chloride that easily produces particles [2].

5.1. Sulphuric acid

The largest fraction of the SO_2 in the atmosphere is oxidized to sulphate in the liquid phase by chemical reactions in cloud droplets. However, a fraction is converted into sulphuric acid in the gas phase by reaction with the hydroxyl radical OH [110,111]. This gas-phase sulphuric acid is the key for most aerosol nucleation events observed in the atmosphere.

The simultaneous measurement of gas-phase H_2SO_4 and nucleation-mode particles in the 3–6 nm size range is shown in Fig. 4. The strong correlation between the two quantities when taking into account a 90 minutes time lag for the growth of the particles to 3 nm size, presents evidence, that sulphuric acid is taking part in the nucleation of the particles [83,112].

Several studies on atmospheric nucleation involving sulphuric acid indicate that the nucleation rate depends on $[H_2SO_4]^n$ with n between 1 and 2 [83,112,113] and therefore, according to Eq. (4) the critical cluster would involve just one or two H_2SO_4 molecules. For $n \leqslant 2$ the nucleation barrier vanishes and the cluster growth would be just kinetically limited from the beginning. Very recently, a cluster activation theory has been proposed to explain this behaviour [112].

Nucleation has rarely been observed in the background stratosphere, and if, then particle formation was observed in the lowermost stratosphere, close to the tropopause [25,114]. It is believed, that the tropical upper free troposphere and tropopause region are the major source regions for the stratospheric background aerosol [22]. Observations of enhanced particle concentration in the stratospheric winter Arctic vortex had been interpreted as indications of binary H_2SO_4/H_2O nucleation [115–119]. However, the enhanced concentrations seem to be rather caused by meteoric smoke particles that are actually nucleated in the mesosphere after the ablation of meteors at $\sim$100 km altitude [4].

A few direct observations of ion-induced nucleation in the atmosphere exist [120–122], as well as indirect indications [53]. Ion-induced nucleation has also been observed to occur in connection with aircraft engine emissions [123,124]. Model calculations show that ion-induced nucleation of sulphuric acid and water may be the dominating
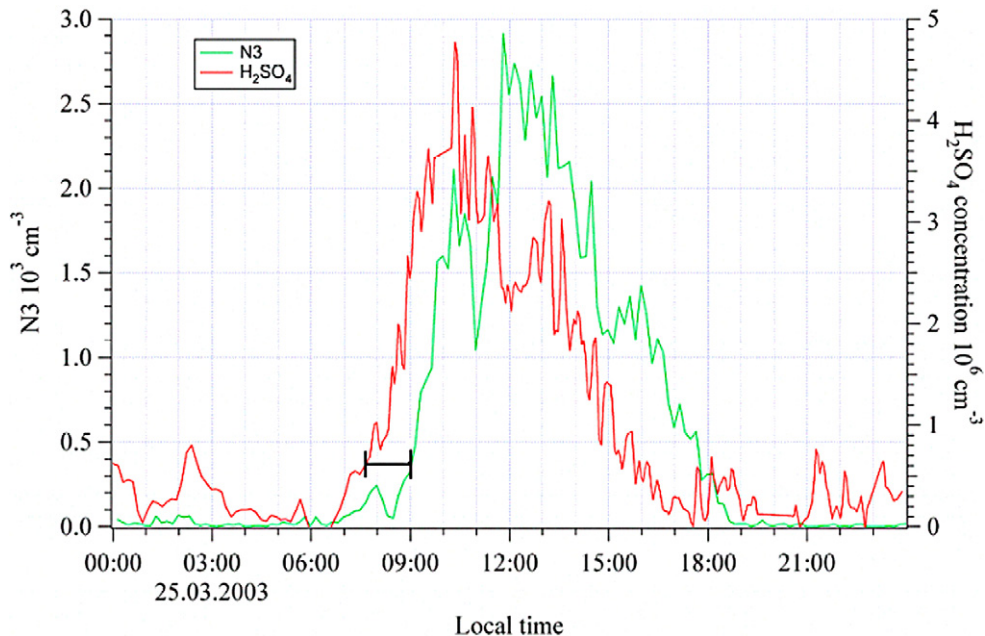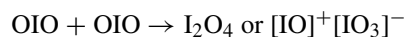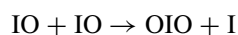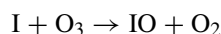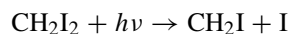

Fig. 4. Gaseous sulphuric acid concentration (H_2SO_4) and number of particles between 3 and 6 nm (N3) during a nucleation event at Hyytiälä (boreal forest). A time lag of about 90 minutes between the two curves exists, the time interval needed for the freshly nucleated particles to grow to observable sizes (>3 nm). From [83].

nucleation process in the free troposphere, despite the fact that the production rate of ion-pairs by galactic cosmic rays is small (<20 cm^{-3} s^{-1}). At ground level it is currently unclear in how far ion-induced nucleation is an important process. Ion clusters have been observed to accompany neutral nucleation events [121], and it has been observed that ion clusters of sulphuric acid do not grow at ground level conditions [125], in agreement with predictions from an ion-induced nucleation model for H_2SO_4/H_2O [54]. At the ground, potentially further compounds besides H_2SO_4 and H_2O take part in ion-induced nucleation processes as well.

5.2. Iodine oxides

Aerosol measurements at Mace Head on the west coast of Ireland revealed the frequent presence of very high concentrations of nucleation mode particles [33]. The total particle concentration during these nucleation events peaked around 1×10^6 cm^{-3} [6]. It was observed that the nucleation events only take place during low tide conditions and with sunlight present. The measurements showed that the nucleation must take place in the shore area followed by rapid growth to observable sizes. Nucleation rates as large as 10^5–10^6 cm^{-3} s^{-1} and growth rates of 0.1–0.36 nm s^{-1} were determined [126]. Studies of the chemical composition of the nucleation mode particles by EDX-TEM revealed iodine as the major component of the nanometre sized particles [93]. Hygroscopicity measurements and measurements of the gaseous H_2SO_4 concentration argued against sulphuric acid as a major component of the nucleation mode particles [126]. From laboratory studies on the nucleating ability of iodine oxides it was proposed by Hoffmann et al. [94] that OIO is the main nucleating agent. Their suggested chemistry scheme, leading to new particles is:

$$CH_2I_2 + h\nu \rightarrow CH_2I + I$$

$$I + O_3 \rightarrow IO + O_2$$

$$IO + IO \rightarrow OIO + I$$

$$OIO + OIO \rightarrow I_2O_4 \text{ or } [IO]^+[IO_3]^-$$

$$I_2O_4 + nOIO \rightarrow \text{particles}$$

The nucleation is thought to happen as a single-component homogeneous nucleation where polymer-like chains of IO–IO$_3$ are built up [94].

Burkholder et al. [150] conducted laboratory studies of the aerosol nucleation of iodine oxides and modelled the gas-phase chemistry as well as the aerosol nucleation processes. They concluded that IO concentrations of >50 pptv were necessary to explain the observed rapid particle formation and growth in the coastal areas. Concentration measurements by long-path Differential Optical Absorption Spectroscopy (DOAS) yielded much lower concentrations of <5 pptv [127–129]. The DOAS measurements, however, average over several kilometres of light path and the chemically active tidal zone spans only a few hundred meters, therefore it was concluded that in local hot-spots of the tidal zone large enough IO and OIO concentrations can be reached to drive the observed nucleation and growth.

Originally, CH_2I_2 produced by macroalgea and released to the atmosphere during low tide was proposed as the substance supplying the iodine. More recent investigations identified molecular iodine I_2 as a much more important precursor substance [130–132].

Currently it is under investigation whether there is also nucleation occurring over the open ocean, certainly much less vigorous but potentially more important for the atmospheric aerosol budget than the coastal production due to the large open ocean areas. The aerosol production from iodine precursors has been reviewed recently [133].

5.3. Organic molecules

Terpenes, emitted by vegetation were discovered to be a source of blue haze aerosol already several decades ago [134]. More recently, nucleation events in forested areas have been observed, for example, in Finland (e.g. [29, 135]), Portugal (e.g. [30]), Canada [31], and Germany (e.g. [32,83,136]). O'Dowd et al. [99] suggested that already the nanometre-sized particles (3–10 nm) produced during nucleation events in a forest in Finland are most likely composed predominantly of organics such as pinic acid or cis-pinonic acid, whereas inorganic substances like ammonium sulphate could be excluded as a major component. In aerosol chamber experiments it was found that the oxidation of monoterpenes ($C_{10}H_{16}$) like α-pinene, β-pinene, sabinene, limonene and sesquiterpenes ($C_{15}H_{24}$) like

β-caryophyllene produces new particles rapidly ([137] and references therein). Oxidation of terpenes proceeds in complex pathways mostly via reaction with ozone O_3, the hydroxyl radical OH or the nitrate radical NO_3 [138–140]. Some low-volatility products are produced in these reactions, e.g. cis-pinic acid [141,142]. In addition to biogenic volatile organic compounds, some aromatic substances, such as toluene, xylene and trimethylbenzene (TMB) are abundantly emitted from anthropogenic sources, for example, as part of gasoline vapours. These aromatic substances are photooxidized in the atmosphere, leading to some low-volatility products which partition into the aerosol phase similar to the terpene products [143,144] and may be able to take part in the nucleation or early growth processes as well. While several field investigations demonstrated that the condensational growth of the freshly nucleated particles in forests can be explained only to a minor degree by condensation of sulphuric acid [32,83,136] and seems to be dominated by condensation of organics [99], it is expected that in the atmosphere the monoterpene concentrations are not sufficient for their low-volatility oxidation products to form thermodynamically stable clusters, i.e., overcome the nucleation barrier. Higher supersaturations of organic acids than can be expected in the ambient atmosphere would be necessary to produce new particles, if no sulphuric acid is present [145]. A current hypothesis is that in the atmosphere often thermodynamically stable molecular clusters of H_2SO_4 and H_2O are formed, on which organics subsequently condense [67]. Alternatively, it has been suggested that the oxidation of sesquiterpenes like β-caryophyllene is potentially able to nucleate particles at atmospheric conditions even without the involvement of inorganic species like sulphuric acid [146]. Similarly, low-volatility diacyl peroxides were also suggested to be important organic nucleating agents [147]. Furthermore, Zhang et al. found that aromatic organic acids like benzoic acid enhance the nucleation rate of sulphuric acid considerably. Their quantum chemical calculations show that a clustering of the organic acids with sulphuric acid yields strongly bonded clusters [145]. Therefore, it is conceivable that the interaction of low-volatility organic acids with sulphuric acid might also be responsible for some of the observed atmospheric nucleation processes. Overall, the question in how far organic substances in the atmosphere can nucleate new particles is still a controversial issue and a topic of current research. In the boundary layer low-volatility organics apparently dominate the growth of freshly nucleated particles frequently.

6. Summary and conclusions

The formation of new aerosol particles is frequently observed in the lower atmosphere at various locations. Freshly nucleated particles contribute substantially to the average total aerosol number and are expected to contribute to the number of atmospheric cloud condensation nuclei [15]. Nucleation is often observed as a burst of new particles being formed during day time as a result of photochemical reactions forming gas-phase products with low-vapour pressures. Emissions from anthropogenic sources supply a large fraction of the key precursor substances for nucleation such as sulphur dioxide as well as ammonia or benzene and toluene. At the same time anthropogenic activities increase the overall atmospheric aerosol burden substantially, providing therefore an increased condensational sink of pre-existing particles that can inhibit nucleation to take place.

The nucleation and the subsequent growth of particles that have overcome the nucleation barrier need to be treated as decoupled processes in the atmosphere, especially in the boundary layer, as low-vapour pressure organic substances that may dominate the growth of the freshly formed particles not necessarily take part in the nucleation and, vice versa, sulphuric acid that is essential for the nucleation often plays a minor role for the subsequent growth. Nevertheless, it has recently been found that some organic acids enhance also the nucleation of sulphuric acid considerably [145].

Observed nucleation rates in the boundary layer are typically in the range of 0.01–$10 \, \text{cm}^{-3} \, \text{s}^{-1}$ and typical growth rates range at 1–$20 \, \text{nm} \, \text{h}^{-1}$ [3].

Our understanding of the nucleation mechanisms is still limited and several discrepancies exist. Sulphuric acid is identified as the key nucleating substance in the atmosphere, except for coastal nucleation events where oxidized iodine compounds, most likely OIO, are probably the nucleating agents. Nucleation of sulphuric acid is enhanced by the presence of water, ammonia and organic acids as well as ions. Recent studies indicate that ion-induced nucleation of sulphuric acid and water is likely to be an important if not the most important nucleation process in the free troposphere [45,54]. In the boundary layer, often neither ion-induced nor homogeneous binary nucleation of sulphuric acid and water seem to be able to explain the observed nucleation events [45,47,54,113]. Here, different, so far undiscovered nucleating agents besides sulphuric acid are needed, or a process involving three, four or even more nucleating substances. Several atmospheric studies show a functional dependence of the nucleation rate with the gas-phase sulphuric acid concentration raised to the power of 1. The nucleation theorem indicates for these cases that

nucleation would be barrierless, every sulphuric acid molecule would grow and its growth is only kinetically limited from the beginning. However, such barrierless nucleation at ground conditions is in disagreement with the laboratory data for the H_2SO_4/H_2O and the $H_2SO_4/H_2O/NH_3$ systems that predicts the critical cluster at 287 K to include ~8 molecules of sulphuric acid [63]. Similarly, predictions of nucleation rates for homogeneous nucleation as well as for ion-induced nucleation of H_2SO_4/H_2O from classical nucleation theory differ by several orders of magnitude from predictions based on measured thermochemistry [45,54,77].

Further research is needed to understand the atmospheric nucleation processes and we are not able to predict the occurrence of atmospheric nucleation events. Field measurements of all involved gas-phase species, of the nucleation mode particles at sizes smaller than 2.5 nm as well as measurement of the chemical composition of the particles are desirable. Further laboratory investigations of nucleation are needed to resolve the existing discrepancies. In these experiments, the existing studies on H_2SO_4/H_2O nucleation have to be checked, further systems such as H_2SO_4 in combination with various carboxylic acids have to be studied and the role of ion-induced nucleation has to be verified. Temperature-dependent nucleation rates in the range of 200–300 K are needed. Furthermore, laboratory investigations to derive more thermochemical data for the relevant neutral and charged clusters are needed, as well as improved vapour pressure data for many organics. Further modelling efforts are needed to overcome the shortcomings of classical nucleation theory. Modelling efforts need to be extended to assess the role of nucleation for the atmospheric aerosol budget, for cloud formation and climate. The influences of anthropogenic activities on atmospheric aerosol nucleation need to be studied. Additionally, the health effects of freshly nucleated particles have to be assessed in detail.

Last but not least, it has been suggested by P.J. Crutzen [148] to study the effects of injecting large amounts of sulphur into the lower stratosphere to form sulphate particles that reflect sunlight and thereby counteract dangerous global warming by greenhouse gases. The effects would be similar to a volcanic eruption like the one of Mt. Pinatubo in 1991. In order to assess the feasibility and the effects as well as to potentially optimise such geo-engineering efforts, also the nucleation of sulphuric acid–water aerosol particles at low temperatures needs to be understood in depth.

Acknowledgements

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