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NUMERICAL APPROACHES TO NEW PARTICLE
FORMATION AND GROWTH IN THE ATMOSPHERE

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Academic dissertation

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Henri Juhani Vuollekoski
University of Helsinki, 2010

Abstract

Aerosols impact the planet and our daily lives through various effects, perhaps most notably those related to their climatic and health-related consequences. While there are several primary particle sources, secondary new particle formation from precursor vapors is also known to be a frequent, global phenomenon. Nevertheless, the formation mechanism of new particles, as well as the vapors participating in the process, remain a mystery. This thesis consists of studies on new particle formation specifically from the point of view of numerical modeling.

A dependence of formation rate of 3 nm particles on the sulphuric acid concentration to the power of 1–2 has been observed. This suggests nucleation mechanism to be of first or second order with respect to the sulphuric acid concentration, in other words the mechanisms based on activation or kinetic collision of clusters. However, model studies have had difficulties in replicating the small exponents observed in nature. The work done in this thesis indicates that the exponents may be lowered by the participation of a co-condensing (and potentially nucleating) low-volatility organic vapor, or by increasing the assumed size of the critical clusters. On the other hand, the presented new and more accurate method for determining the exponent indicates high diurnal variability. Additionally, these studies included several semi-empirical nucleation rate parameterizations as well as a detailed investigation of the analysis used to determine the apparent particle formation rate.

Due to their high proportion of the earth's surface area, oceans could potentially prove to be climatically significant sources of secondary particles. In the lack of marine observation data, new particle formation events in a coastal region were parameterized and studied. Since the formation mechanism is believed to be similar, the new parameterization was applied in a marine scenario. The work showed that marine CCN production is feasible in the presence of additional vapors contributing to particle growth.

Finally, a new method to estimate concentrations of condensing organics was developed. The algorithm utilizes a Markov chain Monte Carlo method to determine the required combination of vapor concentrations by comparing a measured particle size distribution with one from an aerosol dynamics process model. The evaluation indicated excellent agreement against model data, and initial results with field data appear sound as well.

Keywords: new particle formation, modeling, nucleation, particle growth

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List of publications

This thesis consists of an introductory review followed by six peer-reviewed research articles, cited according to their roman numerals in the introductory part. The articles are reproduced with the kind permission of the journals concerned.

- I** Sihto, S.-L., Vuollekoski, H., Leppä, J., Riipinen, I., Kerminen, V.-M., Korhonen, H., Lehtinen, K. E. J., Boy, M. and Kulmala, M. (2009). Aerosol dynamics simulations on the connection of sulphuric acid and new particle formation, *Atmos. Chem. Phys.*, 9:2933–2947.
- II** Vuollekoski, H., Nieminen, T., Paasonen, P., Sihto, S.-L., Boy, M., Manninen, H., Lehtinen, K. E. J., Kerminen, V.-M. and Kulmala, M. (2010). Atmospheric nucleation and initial steps of particle growth: numerical comparison of different theories and hypotheses, *Atmos. Res.*, 98:229–236.
- III** Vuollekoski, H., Sihto, S.-L., Kerminen, V.-M., Kulmala, M. and Lehtinen, K. E. J. (2010). A numerical comparison of different methods for determining the particle formation rate, *Atmos. Chem. Phys. Discuss.*, 10:18781–18805.
- IV** Vuollekoski, H., Kerminen, V.-M., Anttila, T., Sihto, S.-L., Vana, M., Ehn, M., Korhonen, H., McFiggans, G., O’Dowd, C. D. and Kulmala, M. (2009). Iodine dioxide nucleation simulations in coastal and remote marine environments, *J. Geophys. Res.*, 114:D02206.
- V** Ehn, M., Vuollekoski, H., Petäjä, T., Kerminen, V.-M., Vana, M., Aalto, P., de Leeuw, G., Ceburnis, D., Dupuy, R., O’Dowd, C. D. and Kulmala, M. (2010). Growth rates during coastal and marine new particle formation in Western Ireland, *J. Geophys. Res.*, 115:D18218.
- VI** Vuollekoski, H., Boy, M., Kerminen, V.-M., Lehtinen, K. E. J. and Kulmala, M. (2010). MECCO: A Method to Estimate Concentrations of Condensing Organics – Description and Evaluation of a Markov chain Monte Carlo Application, *J. Aerosol Sci.*, 41:1080–1089.

1 Introduction

Aerosols are ubiquitous. While the best-recognized aerosol is undeniably the deodorant, the concept of aerosols is more general – from airport-closing ash clouds to tobacco smoke mixed with the odors of the spring-like forest and from the proprietary content of asthma inhalers to the salty air that rusts sauna stoves by the sea. An aerosol is a mixture of a carrier gas (e.g. air) and particles suspended in it. These particles may be solid or liquid, and of varying chemical composition. Their diameter ranges from the size of a few gas molecules, or about a nanometer, to several micrometers. Particles bigger than this tend to be too heavy as compared to the buoyancy provided by the air, and settle. (e.g. Seinfeld and Pandis, 2006)

While the fine particles may appear inert, they have differing effects on their surroundings. For example, centuries-old buildings stained by soot particles are a saddening sight in several metropolises around the world (e.g. Sánchez et al., 2010). For humans, inhaled particles may pose serious health-related risks when deposited in the respiratory system (Stieb et al., 2002; Brunekreef and Holgate, 2002; Nel, 2005; Hänninen et al., 2009). In fact, the World Health Organization (2006) estimates that yearly 2 million people in the world die because of air pollutants (excluding tobacco smoke). On the other hand, the aerosol content bursting out of asthma inhalers is a relief to many (e.g. Haughney et al., 2010). Sometimes, or actually increasingly often in polluted cities, the concentration of particles in air may be so high that it decreases visibility (Cabada et al., 2004; Bäumer et al., 2008; Wang et al., 2009).

Recently, the climatic importance of particles has become a subject of increasing interest in research groups around the globe. Or rather, the debate goes around how important the aerosol effects actually are for the climate. While some particles, especially those consisting of soot, warm the climate directly by absorbing sunlight, most cool the planet by reflecting sunlight back to space (e.g. Cabada et al., 2004). Perhaps the most interesting aspect is the indirect effect of the particles that get to act as cloud condensation nuclei (CCN): they affect the formation of clouds, their lifetime and albedo, which then determine the shade provided by clouds as well as the amount and distribution of rainfall, influencing the water cycle and fresh water resources (Rosenfeld, 2000; Ramanathan et al., 2001; Kerminen et al., 2005; Rosenfeld et al., 2008). Although the net aerosol effect is generally agreed upon by climate scientists to be planet-cooling, the level of uncertainty associated with it roughly equals the total pos-

itive radiative forcing caused by carbon dioxide (Intergovernmental Panel on Climate Change, 2007).

One of the greatest unknowns related to aerosols is the formation of new particles in the atmosphere. While there are plenty of primary sources from volcanic activity to desert dust, Kulmala et al. (2004) showed that secondary particle formation by nucleation from precursor vapors is a frequent and global phenomenon. Several studies have suggested that sulphuric acid may be the key vapor with linear or quadratic proportionality between its concentration and the formation rate of new particles (Weber et al., 1996; Kulmala et al., 2006; Sihto et al., 2006; Riipinen et al., 2007; Kuang et al., 2008; **Paper I**). Explanations to this include sulphuric acid induced activation of pre-existing clusters (Kulmala et al., 2006) and kinetic collision of two clusters containing a sulphuric acid molecule (McMurry and Friedlander, 1979), although **Papers I-II** found that the mentioned relation may also be significantly affected by assumptions made in the analysis, such as the presence of a co-condensing organic vapor or the size of the critical cluster. Nevertheless, these findings are in clear contrast with e.g. the binary (Vehkamäki et al., 2002) and ternary (Napari et al., 2002) nucleation theories that predict 4–10 sulphuric acid molecules in the critical cluster that is needed for a stable particle to form.

Under certain conditions vapors other than sulphuric acid may be of equal or even greater importance for new particle formation to occur. For example, a strong correlation between iodine vapor emissions and bursts of new particles has been observed in coastal regions, especially at the Irish west coast (O’Dowd and Hoffmann, 2005; Yoon et al., 2006; O’Dowd and De Leeuw, 2007). Due to the availability of these vapors in remote marine conditions, and the fact that more than 70% of the Earth’s surface is covered by oceans, the concerned nucleation mechanism may be of significant global importance (e.g. Pechtl et al., 2006; O’Dowd and De Leeuw, 2007; **Paper IV**). Nevertheless, few observations of purely marine nucleation have been reported (**Paper V**).

Over land, an increasing number of studies have reported evidence of organic vapors contributing to new particle formation (O’Dowd et al., 2002a; Bonn et al., 2008; Smith et al., 2008; Paasonen et al., 2009). Especially the growth rate of the just-formed particles tends to top that which could be attributed to condensation of sulphuric acid alone (Weber et al., 1997; Birmili et al., 2003; Boy et al., 2005; Fiedler et al., 2005; Stolzenburg et al., 2005; Iida et al., 2008), implying that very low-volatility organic

vapors participate in the very earliest steps of new particle formation. However, it remains to be discovered whether these organics are only condensing on the freshly nucleated particles, or if they actually play a role in the nucleation itself (**Paper III**).

A common difficulty in the investigation of new particle formation mechanisms is, with the exception of sulphuric acid, the uncertainty related to the participating vapors: the lack of accurate measurements of their concentration and detailed information of their chemical properties and identity. Additionally, the determination of atmospheric nucleation rates is currently inaccurate in spite of the recent progress in measuring atmospheric clusters and nanometer-sized particles (Sipilä et al., 2008; Iida et al., 2009; Lehtipalo et al., 2009; Manninen et al., 2009b). Unfortunately, some of these questions have to wait for sufficient advances in measurement instrumentation.

However, direct measurements are not always necessary, as many unknown topics can be addressed by means of computer simulations and data analysis. The information acquired in this way may help in forming theories and hypotheses that can usually be put to test in accordance with measurable quantities. Often, the analysis starts from measurement data (**Papers II, IV, V**), but it may also involve model output data (**Papers I-VI**). Because many of these techniques include considerable amounts of human labor, automation should be endorsed whenever possible (**Papers II, III, VI**).

This thesis aims at improving our knowledge and capabilities on the following subjects:

- to deepen the understanding of the connection between new particle formation and the vapors affecting it (**Papers I-V**)
- to provide semi-empirical parameterizations for several nucleation mechanisms in boreal forest, coastal and marine environments (**Papers II, IV**)
- to develop new and more accurate numerical methods for use in aerosol science (**Papers II, III, VI**)

2 Formation and growth of new particles in the atmosphere

New particle formation has been observed globally in various environments (Kulmala et al., 2004), but the studies in this thesis have utilized field data from two research stations. The first one is the SMEAR II (Station for Measuring Forest Ecosystem – Atmosphere Relations, Hari and Kulmala (2005)), a world-widely recognized research station located in a boreal forest environment in Hyytiälä, Finland (**Papers I, II, VI**), and the second one the Mace Head Atmospheric Research Station on the Irish west coast (**Papers IV, V**). Additionally, **Paper V** investigates data acquired onboard the research vessel Celtic Explorer. While the environments and present conditions differ greatly, the general characteristics of new particle formation events observed around the world are mainly in conformity with each other: a burst of new particles is observed, followed by their subsequent growth to larger sizes.

The mentioned research facilities house numerous scientific instruments, but only the ones most relevant for the work done in this thesis are mentioned here. Data from the DMPS (differential mobility particle sizer, Aalto et al. (2001)) provides the size distribution of particles 3–1000 nm in diameter. The NAIS (neutral cluster and air ion spectrometer, Manninen et al. (2009b)) on the other hand, gives the size distribution of both neutral and charged particles 1.8–40 nm in diameter. Finally, the CIMS (chemical ionization mass spectrometer, Petäjä et al. (2009)) is able to measure the gaseous sulphuric acid (H_2SO_4) concentration in air.

An example of a new particle formation event recorded by the DMPS from a 24-hour period on 7 May 2007 in Hyytiälä is presented in Figure 1, and it displays many common properties visible in particle size distribution data. First of all, there is a “background” particle mode, an Aitken mode, that started around 60 nm in the first hour of the day and during the day grew closer to 100 nm. At about 10:00 the DMPS began recording new particles that apparently had grown to a detectable size (3 nm). This new particle formation event lasted until about 14:00, but the new particles kept growing until this nucleation mode fused into the Aitken mode.

Figure 2 displays NAIS data from the same day as Figure 1, and one may easily notice the similarities. Note that the average concentrations recorded by the NAIS instrument are significantly higher than those by the DMPS – the absolute concentrations of the

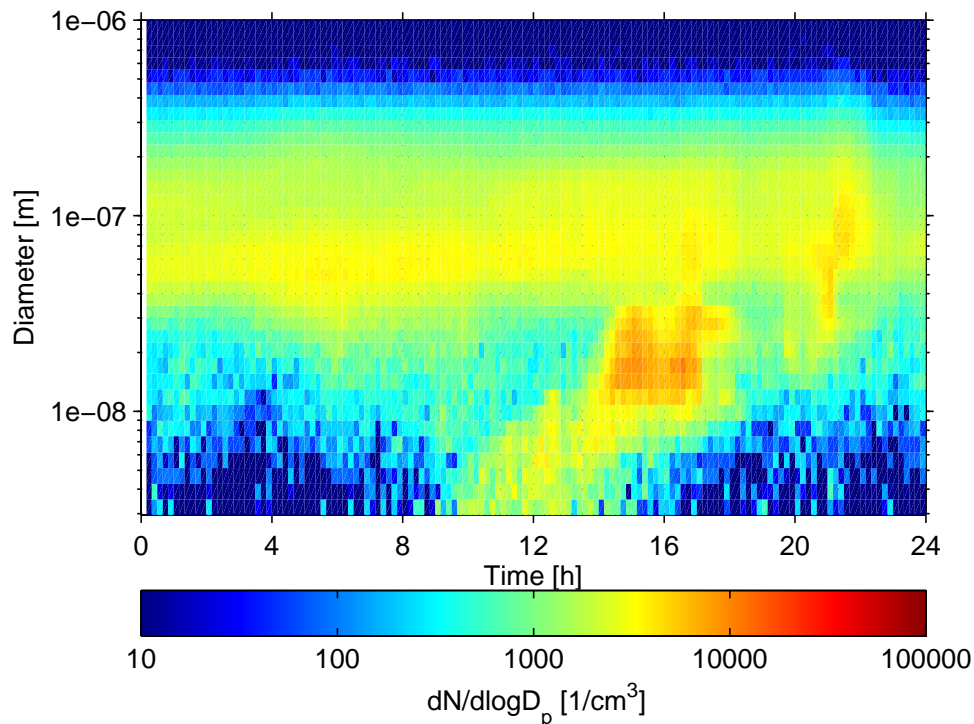


Figure 1: A new particle formation event recorded by the DMPS instrument on 7 May 2007 at the SMEAR II station.

NAIS are typically 2–3 times too high (Manninen et al., 2009a). Nevertheless, the advantage of the NAIS is clear: the measurements reach “deeper” into the nucleation. Indeed, the data reveals a pool of clusters below 2 nm (Kulmala et al., 2007; Lehtipalo et al., 2009) that at around 10:00 activates and begins to grow – the concentration of the clusters appears to have decreased during new particle formation.

To further investigate the new particle formation event on 7 May 2007, it is useful to study the vapor concentrations on that day, see Figure 3. The sulphuric acid concentration was measured by the CIMS instrument, and the low-volatility organic vapor was estimated from particle growth rates (Paasonen et al., 2010). They both had a roughly sinusoidal diurnal behavior in accordance with having been produced via oxidation by the OH radical formed by the photochemistry initiated by sunlight (e.g. Paasonen et al., 2009). This diurnal behavior is also visible in the particle growth rates in Figures 1 and 2. However, new particle formation only occurred when the sulphuric acid and low-volatility organic concentrations exceeded 10^6 and 10^7 molecules cm^{-3} , respectively. It should be noted that these vapors only explain the growth of 2–4 nm

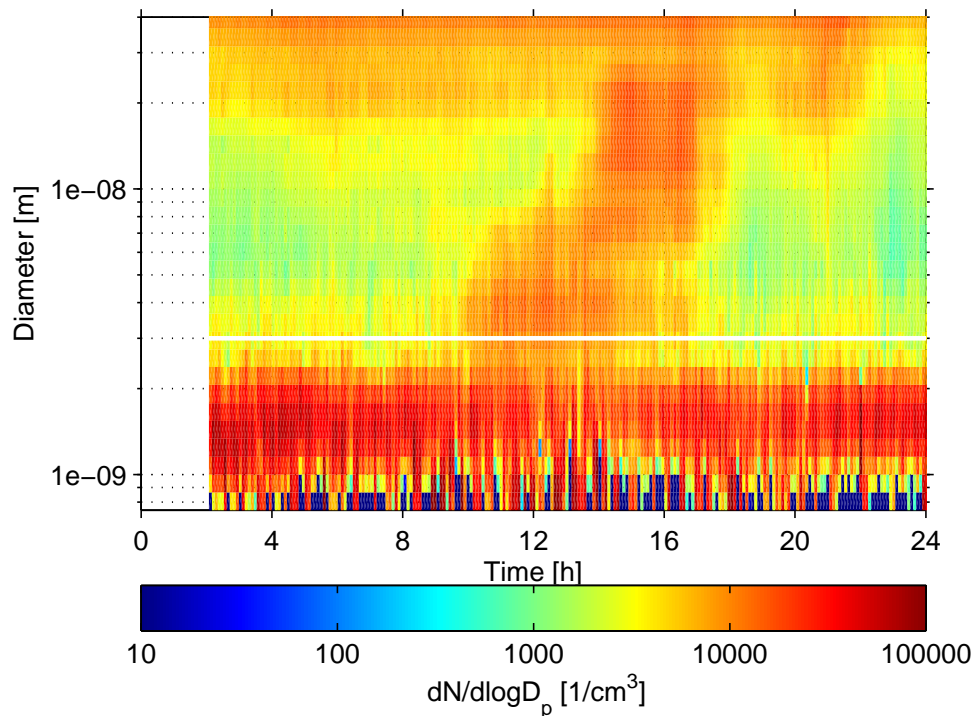


Figure 2: A new particle formation event recorded by the NAIS instrument on 7 May 2007 at the SMEAR II station. The white horizontal line at 3 nm depicts the lower detection limit of the DMPS. Note that the theoretical detection limit of NAIS is about 1.8 nm, and particle readings below this are unreliable. (Data is missing from the first two hours.)

particles, and e.g. the growth of the Aitken mode requires additional vapors with higher volatility (**Paper II**).

Statistically, a new particle formation event has been observed at SMEAR II on one fourth of days (Dal Maso et al., 2005). However, nearly half of the days remained undefined or missed data, and Dal Maso et al. (2005) actually found that the ratio of event to non-event days is close to even. In Mace Head, new particle formation is observed slightly more often than not (Yoon et al., 2006). At both stations, spring periods exhibit the most frequent new particle formation events, but the detailed reason for this remains unknown.

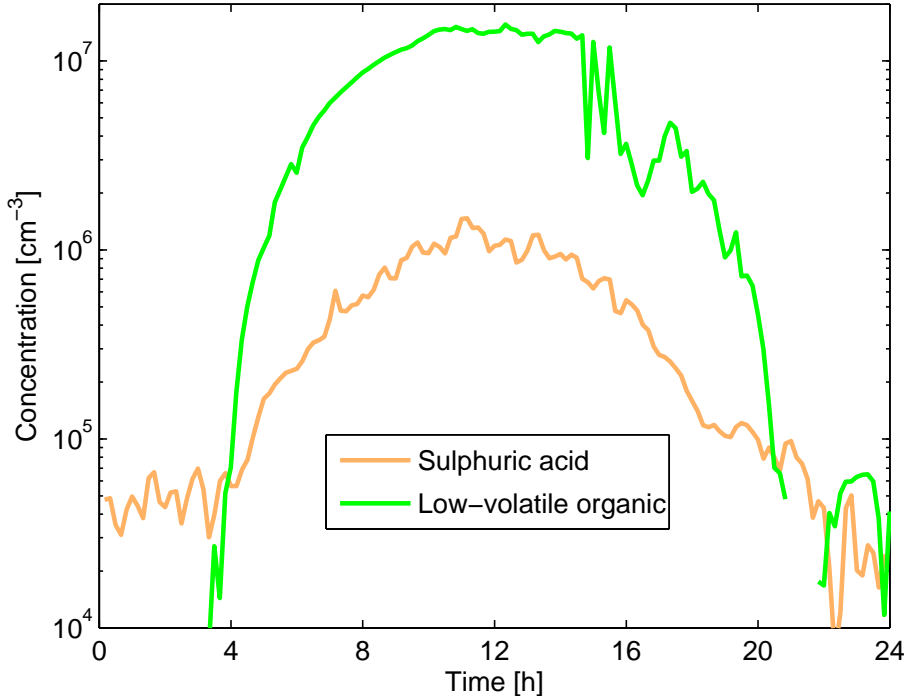


Figure 3: The measured sulphuric acid concentration and the estimated low-volatility organic vapor concentration on 7 May 2007 at the SMEAR II station.

2.1 Aerosol dynamics

Various processes relate to the formation and growth of new particles. First they form by nucleation from precursor vapors. Once formed, they may collide with each other and coagulate, grow/shrink due to condensation/evaporation of vapors, or are removed by e.g. depositing on the ground. Additionally, their composition may change due to chemical reactions.

Because the number concentration and size (i.e. volume v and mass m if we know the density) of particles are relatively easy to measure, and yet quite practical quantities, it is useful to give an equation for the time evolution of particle size distribution. If we define the particle volume distribution function $n(v, t) = \partial N / \partial v$, where t is time and N the cumulative number concentration of particles, we can form the continuous general dynamic equation (GDE), which in its somewhat simplified form states (e.g. Seinfeld and Pandis, 2006):

$$\begin{aligned} \frac{\partial n(v, t)}{\partial t} &= \frac{1}{2} \int_0^v K(v - q, q) n(v - q, t) n(q, t) dq - n(v, t) \int_0^\infty K(q, v) n(q, t) dq \\ &- \frac{\partial}{\partial v} [(p_k - \gamma_k) v_1 n(v, t)] + J_{nuc}(t) \delta(v - v_0) + S(v, t) - R(v, t). \end{aligned} \quad (1)$$

Here, $K(v, v')$ is the coagulation coefficient between particles of volumes v and v' , p_k and γ_k are the rates at which a k -mer gain or lose a monomer due to condensation or evaporation, v_1 is the volume of the condensing/evaporating monomer, J_{nuc} is the nucleation rate, δ is the delta function, v_0 is the volume of the critical cluster, and S and R represent additional sources and losses, such as primary particular sources and deposition. The work done in this thesis is mainly related to two of these processes: nucleation and condensation.

Nucleation is a phase transition, in which the atoms or molecules of a supersaturated vapor combine to form a critical cluster, or “seed”. The cluster is critical in the sense that a smaller one would not be stable and it would break apart to reach the minimum of energy. On the other hand, it is willing to grow (see below). Various theories exist on how the clusters are formed, and which vapors contribute in this process. It is agreed upon, however, that sulphuric acid is important for new particle formation, at least in continental regions.

The binary nucleation scheme involving water and sulphuric acid (e.g. Kulmala et al., 1998; Vehkamäki et al., 2002) has been applied extensively. However, the measured sulphuric acid concentrations are rarely enough to predict the observed nucleation rates in tropospheric conditions (Weber et al., 1996). The ternary nucleation of sulphuric acid, ammonia and water (Korhonen et al., 1999; Napari et al., 2002) solved this problem: the inclusion of ammonia reduces the required level of sulphuric acid; even too much according to some reports (e.g. Ball et al., 1999; Lucas and Akimoto, 2006; **Paper I**). However, the binary and ternary nucleations predict 4–10 sulphuric acid molecules in the critical cluster, which is in clear contrast with the observed 1–2 (Weber et al., 1996; Kulmala et al., 2006; Sihto et al., 2006; Riipinen et al., 2007; Kuang et al., 2008; **Paper I**). Also, Riipinen et al. (2007) found no correlation between ammonia and new particle formation. Nevertheless, new parameterizations of ternary nucleation have increased its agreement with the measurements (Merikanto et al., 2007).

Electrodynamics offer another view: it has been proposed that nucleation around a charged kernel would facilitate the formation of critical clusters (Raes and Janssens,

1985, 1986), and a model study by Yu et al. (2008) even suggests that ion-mediated nucleation is the main mechanism leading to new particle formation. However, recent experimental studies suggest that the contribution of ion-induced nucleation varies from less than 1% in Mexico City (Iida et al., 2008) to 6%–15% in Hyytiälä (Gagne et al., 2008; Boy et al., 2008) and up to 27% in Jungfraujoch, Germany (Manninen et al., 2010). Nevertheless, ions were not considered in this thesis.

Because of the observed linear or quadratic dependence of nucleation rate on sulphuric acid concentration (Weber et al., 1996; Kulmala et al., 2006; Sihto et al., 2006; Riipinen et al., 2007; Kuang et al., 2008; **Paper I**), and the observed ever-present cluster pool around 1.5 nm in diameter (Kulmala et al., 2007; Lehtipalo et al., 2009), two simple nucleation mechanisms have become more and more popular. These are the so-called kinetic nucleation (McMurry and Friedlander, 1979) of two colliding clusters containing one sulphuric acid molecule, and the cluster activation theory (Kulmala et al., 2006), in which clusters containing one sulphuric acid molecule are “activated” for further growth by heterogeneous nucleation, heterogeneous chemical reactions or activation of soluble clusters.

On the other hand, because the temporal behavior of sulphuric acid concentration is mainly due to the diurnal behavior of the OH concentration, the diurnal behavior of the concentrations of oxidation products of some volatile organic compounds may also share the characteristic shape of sulphuric acid concentration. It is therefore reasonable that the above mentioned correlation between particle formation rate and sulphuric acid concentration could also be explained by these low-volatility organics, meaning that instead of 1–2 sulphuric acid molecules in the critical cluster, there could also be 1–2 organic molecules, or both. Indications of significant organic contribution to the composition and growth of nucleation mode particles has indeed been reported (Bonn et al., 2008; Smith et al., 2008; Paasonen et al., 2009), which does not necessarily imply contribution in the nucleation, though. Such nucleation mechanisms arising from this idea have been compared against measurements and parameterized, and they have proven themselves feasible (Paasonen et al., 2010; **Paper II**).

In coastal environments, iodine vapors have been found to correlate with new particle formation (O’Dowd and Hoffmann, 2005; O’Dowd and De Leeuw, 2007), and the measured levels of sulphuric acid are too low to explain the observed, very high particle formation rates. **Paper IV** investigates the possibility of iodine dioxide participating in new particle formation and growth by assuming linear or quadratic dependence on its

concentration i.e. via similar nucleation mechanisms as discussed above. Because the same iodine vapors could be formed also at remote marine environments (Yamamoto et al., 2001; Pechtl et al., 2006), and because of the fact that the majority of the earth’s surface is covered by oceans, this rarely measured “iodine induced nucleation” may be of great climatic importance, (O’Dowd and De Leeuw, 2007; **Papers IV-V**).

The general equations for the cluster activation and kinetic nucleation mechanisms are

$$J_{nuc} = A \times [\text{vapor}] \tag{2}$$

$$J_{nuc} = K \times [\text{vapor}]^2, \tag{3}$$

where A and K are the semi-empirical activation and kinetic coefficients, and [vapor] signifies the concentration of the nucleating vapor, or a linear combination of such vapors. The coefficients depend on some currently unknown ambient conditions (Paasonen et al., 2009). For the parameterizations performed in this thesis (**Papers II, IV**), as well as in all model runs, the coefficients were assumed constant.

Note that even though the constants A and K could be chosen so that the nucleation rates at some vapor concentration match, changes in vapor concentration make the nucleation rates vary. Examples of normalized nucleation rates using the vapor concentrations presented in Figure 3 are plotted in Figure 4. From the figure the difference between linear and quadratic nucleation rates is obvious, as well as the fact that the nucleating vapor is difficult to discern, if the diurnal behaviors of the vapors are similar.

Condensation and evaporation are processes that strive to an equilibrium between the particles and ambient vapors that surround them. The atoms and molecules of gases are in constant motion, sometimes causing them to collide into the particle. The ratio of the vapor pressure and its saturation vapor pressure determines whether they are absorbed, in which case the particle grows. In the opposite case the particle shrinks due to evaporating vapor atoms and molecules. Condensation is a theoretically well-known phenomenon, but the vapors condensing, as well as their properties, are often unknown.

The rate of change in the volume of a particle due to the condensation/evaporation of vapor species i can be described by the condensation equation (e.g. Seinfeld and Pandis, 2006)

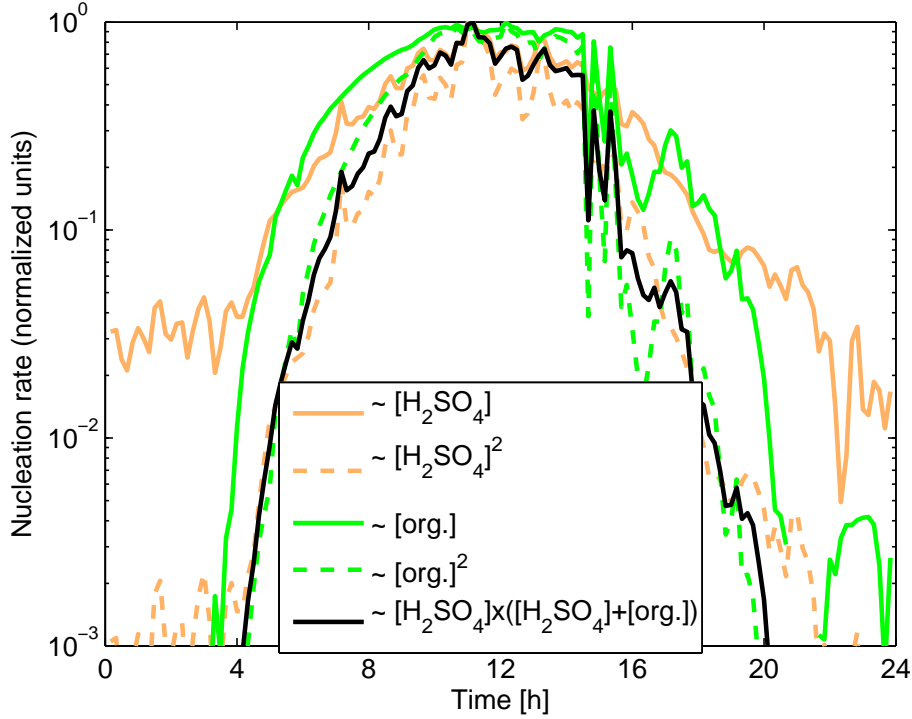


Figure 4: Examples of normalized nucleation rates using the vapor concentrations in Figure 3.)

$$\frac{dv}{dt} = \frac{2\pi D_p M_i}{\rho_p} (c_{\infty,i} - c_{eq,i}), \quad (4)$$

where D_p and ρ_p are the diameter and density of the particle (assumed spherical), M_i is the molecular mass of the condensing vapor atom/molecule, $c_{\infty,i}$ their concentration far from the particle and $c_{eq,i}$ is its equilibrium (saturation) concentration on particle surface.

The saturation vapor pressure is determined first by the saturation vapor pressure over flat surface, $c_{s,i}$, which is a property of the vapor. If the particle consists of a solute, $c_{eq,i}$ will be affected by this according to Raoult's law. From the point of view of this thesis, however, a more interesting factor comes from the Kelvin effect: the saturation vapor pressure is exponentially increased over a curved surface (e.g. Seinfeld and Pandis, 2006)

$$c_{eq,i} = c_{s,i} \exp\left(\frac{4\sigma_i M_i}{RT\rho_i D_p}\right). \quad (5)$$

Here, σ_i and ρ_i are the surface tension and liquid-phase density of the condensing vapor, R is the gas constant and T is the temperature. This Kelvin term is especially important below 10 nm (see Figure 5), and limits the condensation of volatile vapors on small particles. The Kelvin effect was included in all model runs in this thesis, and **Paper VI** makes additional use of its size-dependence.

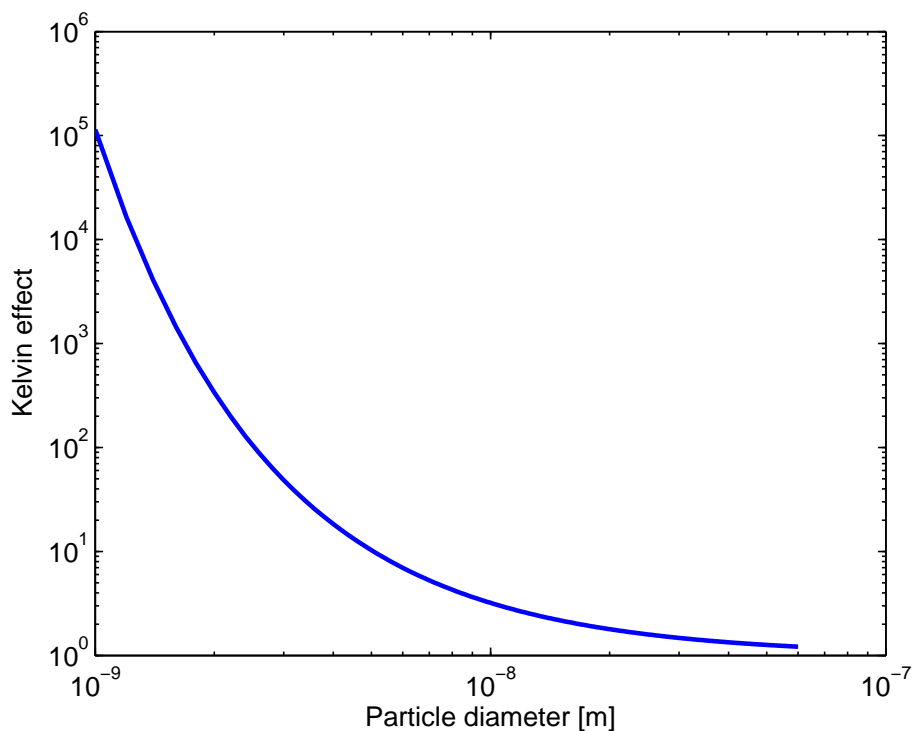


Figure 5: The Kelvin effect as a function of particle diameter for a representative organic vapor ($M=150$ g/mol, $\sigma=0.05$ N/m, $\rho=1107$ kg/m³).

2.2 A modeler's perspective

In spite of the constant advances in computing technology, and the rapid fall in its financial costs, Nature will remain too complex to model accurately, at least in the foreseeable future. In order to include all processes mentioned in the previous chapter,

and some other details, in an aerosol dynamics model, several assumptions and simplifications have to be made. For example, all work in this thesis assumed that the particles are perfectly spherical, although their shape may be quite varying in reality (e.g. Adachi et al., 2010). Likewise, the computational burden imposed by the number of equations must be decreased. An example of this is using constant coefficients in Equations 2-3, which was a general assumption in this thesis. As it is impossible to model the infinitesimal changes due to continuous time, differential equations have to be solved numerically with a finite time step, which must be chosen carefully.

A great difficulty arises from the continuity of the particle size spectrum, and therefore the equations describing its behavior. The continuity is best described in a modal model, which assumes that the particles can be divided into log-normal modes (Whitby and McMurry, 1997; Pirjola et al., 1999). Although this approach is computationally very efficient and quite successful in describing particle growth, it has some issues. Most importantly, in the presence of condensing vapors, all modes grow in size. This creates a dilemma: where should the newly formed particles be allocated? One may of course create a new nucleation mode, but soon the computational burden of many modes will become too heavy. Modal models also have problems in describing coagulation (Seigneur et al., 1986; Zhang et al., 1999), but remain popular in global models due to their computational efficiency.

Another possibility is to divide the particle size distribution in sections. **Papers I-V** applied the fixed sectional approach (Gelbard et al., 1980), which keeps the associated particle size of each section constant. Thanks to this accurate size-resolution, the fixed sectional approach excels in describing all processes with the exception of condensation: since each particle is given the size of its section, particles that grow (according to Equation 4) in between sections must be divided among the two. After the next timestep, some of the particles are already located in the third section, though in reality they might not have grown even to the size of the second section. This nuisance is known as “numerical diffusion” due to its property of widening the particle size distribution (Seigneur et al., 1986; Korhonen et al., 2003). In **Paper VI**, particle growth was modeled more accurately by combining the fixed sectional approach with a moving sectional approach that adjusts the size of sections according to particle growth (Gelbard, 1990; Kim and Seinfeld, 1990).

If the model implementation, and the included physics, chemistry, biology, etc., are sound, the simulation output data may prove to be extremely useful. This is because

the size and time resolutions of the data can be set rather arbitrarily, thereby potentially enhancing the accuracy of the analysis carried out using it. Model data is also free of (unpredictable) noise. But perhaps most importantly, the environmental conditions and parameters of the model can be set freely. Model runs can be performed regardless of wind direction or rain, for example, and if there is a power cut during the simulation, it is repeatable.

All studies included in this thesis utilized development versions of the University of Helsinki Multicomponent Aerosol model (UHMA, Korhonen et al. (2004)), a sectional aerosol dynamics model incorporating all basic aerosol physics: nucleation, condensation, coagulation and deposition. The UHMA model was originally developed for studies of tropospheric new particle formation in Hyytiälä, and has been found to capture their qualitative behavior well (Korhonen et al., 2004).

3 Studies on particle formation rate

Because of the inability of current instrumentation technology to measure the nucleation rate J_{nuc} accurately, nucleation has often been investigated indirectly via a quantity dubbed the (apparent) formation rate of 3 nm particles:

$$J_3 = n_3 \times GR_3 = \left. \frac{\partial N}{\partial D_p} \right|_3 GR_3, \quad (6)$$

where $n_3 = \left. \partial N / \partial D_p \right|_3$ is the size distribution function at 3 nm, and $GR_3 = \left. dD_p / dt \right|_3$ is the growth rate of particles at 3 nm, representing the term $(p_k - \gamma_k)v_1$ in Equation 1: the growth due to condensation and shrinkage due to evaporation.

The logic behind the apparent formation rate is that the particles formed at, for example, 1.5 nm would still be observable at 3 nm; indeed, Kerminen and Kulmala (2002) presented a function to connect these two quantities. The problem, however, is that the precise size of the critical clusters is unknown, as are the vapors responsible for the initial growth of the particles. Also, as the formation rate is a flux quantity, its determination can be cumbersome. Therefore, the number concentration of 3–6 nm particles, N_{3-6} , is sometimes studied instead. Owing to their rapid growth and effective coagulation with the background particles, the existence of these small particles is a good indicator of recent new particle formation.

While Equation 6 can be discretized quite accurately, its accurate determination from field data is very difficult. There are other ways of estimating the apparent formation rate using e.g. N_{3-6} (Sihto et al., 2006; Riipinen et al., 2007), but until **Paper III**, these had not been extensively compared with each other. The study showed reasonably good agreement between the tested methods. Nevertheless, an easily applied and yet considerable improvement in the analysis was suggested.

Being able to determine the apparent formation rate is important in researching properties of the nucleation mechanisms. As already mentioned, several studies have found simple, empirical relations connecting the ambient sulphuric acid concentration and both the number concentration of 3–6 nm particles as well as the formation rate of 3 nm particles (Weber et al., 1996; Sihto et al., 2006; Riipinen et al., 2007; Kuang et al., 2008; Paasonen et al., 2010):

$$N_{3-6}(t) \sim [H_2SO_4]^{pN36}(t - \Delta t_{N36}(t)), \quad (7)$$

$$J_3(t) \sim [H_2SO_4]^{pJ3}(t - \Delta t_{J3}(t)), \quad (8)$$

where Δt are the time delay between the formation of particles and their subsequent detection in particle flux at 3 nm (or concentration at 3–6 nm). Practically all field measurements, as well as the more recent laboratory experiments (e.g. Metzger et al., 2010; Sipilä et al., 2010), suggest the exponents p to be within the range of 1–2, supporting the first and second order nucleation mechanisms covered by Equations 2-3 over the binary or ternary nucleation schemes. Examples of the formation rate at 3 nm, as well as the number concentration of 3–6 nm particles, on our sample day are presented in Figure 6.

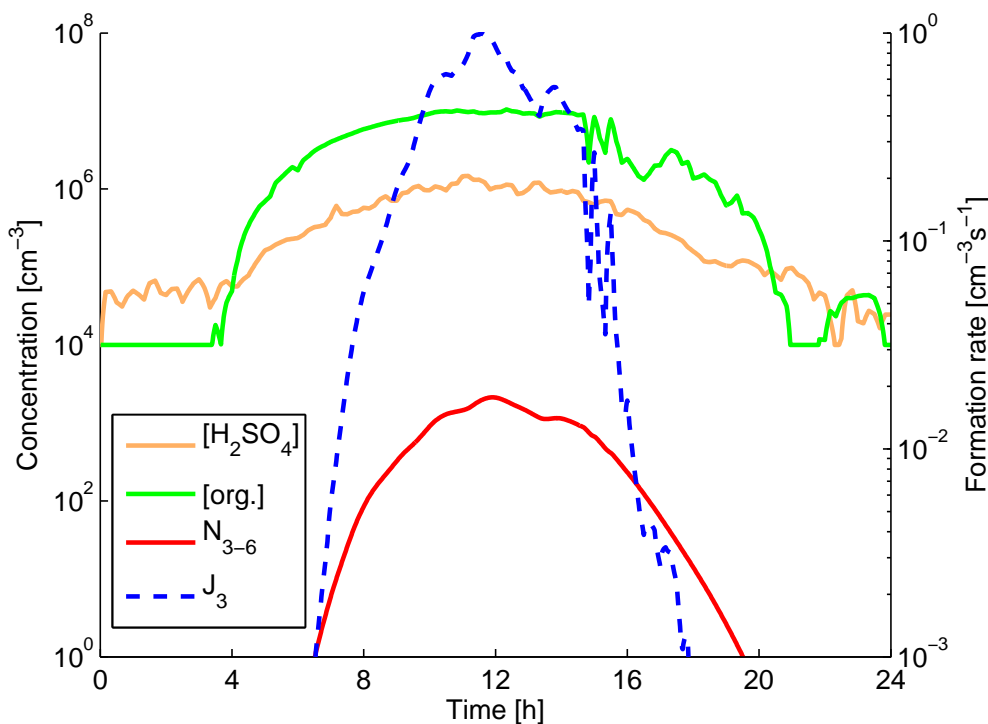


Figure 6: Examples of concentrations of sulphuric acid and a low-volatility organic vapor, concentration of 3–6 nm particles and formation rate of 3 nm particles determined from model output data. In this simulation, new particles were formed via the kinetic nucleation of sulphuric acid (Equation 3).

According to model calculations, the connections implied by Equations 7-8 depend on the applied nucleation mechanism (**Papers I-II**), but the exponents usually exceed those predicted by the nucleation mechanism. This phenomenon was investigated in more detail, and it was found that in order to decrease the exponents attained from data analysis, certain assumptions had to be made. Firstly, the exponent is lowered by the presence of a low-volatility organic vapor. Secondly, the assumed size of the critical clusters affects the exponents: the closer the size of the critical cluster is to 3 nm, the more accurately the features of the nucleation rate are conserved. It should also be noted that due to the change in the importance of different processes, the exponents are different in the morning as compared to afternoon. In general, model calculations based on the cluster activation appear to provide exponents closer to those observed in experimental studies (1–2).

The application and interpretation of Equations 7-8 is complicated by two things, however. Firstly, the very earliest steps in the formation of observable particles seem to be influenced not only by sulphuric acid but also by some low-volatility organic vapors (Paasonen et al., 2009, 2010; Metzger et al., 2010). Secondly, the concentrations of these vapors are expected to have a substantial temporal variability e.g. because of the diurnal cycle of the photochemically driven production. Therefore, the particle growth rate and the time delay, Δt , should vary in time as well. In **Paper II**, a new method to determine the time-varying time delay is presented, which is then further studied in **Paper III**.

4 Peculiarities of coastal new particle formation

When low tide periodically reveals the wet rocks on the waterline approximately 100 m from the Mace Head Atmospheric Research Station during sunlit hours, the macro algae growing on them are exposed to the ambient ozone and emit iodine vapors (McFiggans et al., 2004; O’Dowd et al., 2002c). At least one of their reaction products, iodine dioxide (OIO), is believed to be an important precursor vapor for new particle formation (O’Dowd and De Leeuw, 2007). Due to this extremely localized source, coastal new particle formation has some quite unique features.

Firstly, if the wind is blowing at e.g. 10 m/s from the sea, it takes 10 s for the air to travel the 100 m distance from the shoreline to the measurement station. If new particle formation is detected, and it is not originating from the ocean, the 10 s has been enough (assuming instant acceleration) for the chemical reactions that form OIO from the precursor iodine vapors to occur, for nucleation, and for particle growth. If the largest sized new particles observed were 10 nm in diameter, the average growth rate would be as high as 1 nm/s, or 3.6 $\mu\text{m}/\text{h}$. In reality, the wind speeds recorded during new particle formation events are usually somewhat lower, but the initial particle growth rates close to the shoreline remain on the order of 0.1–1 $\mu\text{m}/\text{h}$ (O’Dowd et al., 2002b; **Paper V**), i.e. very high as compared to usually 2–10 nm/h in Hyytiälä (Kulmala et al., 2004).

Secondly, the distribution of the specific species of algae on the shoreline act as a line or even a point source for the precursor vapors. This means that the air mass passing the shoreline is far from homogeneous, and both the emitted vapors as well as new particles will dilute rapidly. To account for this effect, **Papers IV–V** applied the Pasquill-Gifford dilution parameterization (Gifford, 1961). A schematic of the processes inherent to coastal new particle formation is presented in Figure 7.

Because of the properties described above, modeling of coastal new particle formation has to be put into practice from a different perspective as compared to continental areas. A “normal” simulation would simply describe the evolution of a single air mass. This Lagrangian approach is fine as long as the simulated air mass stays more or less homogeneous, as is assumed in e.g. Hyytiälä. However, in the windy conditions of our coastal example, the observed, consecutive air masses have a newly formed component that was formed at most 10 s earlier. The simulation approach suitable for this scenario is called Eulerian: the coordinate system is fixed in space. Here, the output of each

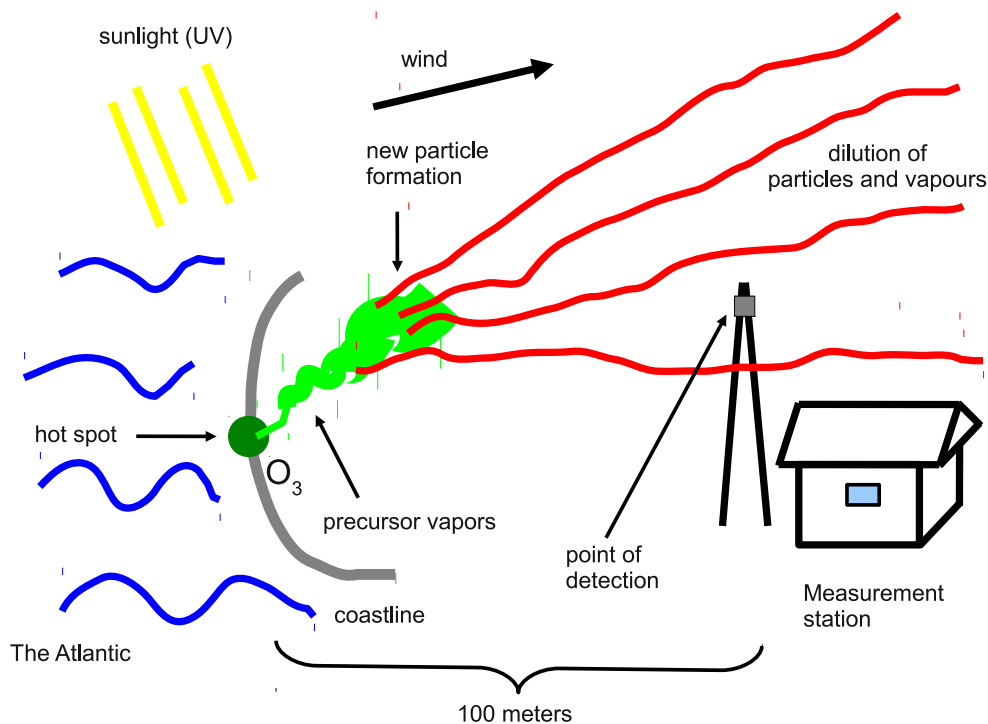


Figure 7: Schematic of coastal new particle formation.

simulation cycle represents only one recorded instant, and adjacent cycles form data that span for the duration of the “experiment”, and is then comparable with the observations from a fixed measurement point. Coastal Lagrangian simulations were carried out in **Paper IV** only, whereas the Eulerian approach was applied in both **Papers IV and V**.

Finally, the shape of the Irish coast near Mace Head (see Figure 8) is complex enough to allow several kinds of “passes” by a shoreline. This means that the new particles observed at the Mace Head Atmospheric Research Station may have been formed due to precursor vapors emitted on a shoreline far away, thereby allowing for substantially longer growth times. Whereas **Paper IV** focused on finding a nucleation parameterization in the simplest of cases, **Paper V** studied also the possibility of the studied air masses having crossed two shorelines, allowing the new particles to grow to significantly larger sizes.



Figure 8: A map of the surrounding regions of the Mace Head Atmospheric Research Station located at the Irish west coast.

5 The Markov chain Monte Carlo method

Mathematics has found ways to derive properties of an unknown physical system based on its statistical properties. The Monte Carlo methods are algorithms that by applying certain rules find order in randomness, originally developed within the Manhattan Project (Fermi and Richtmyer, 1948; Metropolis and Ulam, 1949). The list of potential applications is long, but the studied system has to fulfill the criteria of Markov chains. In essence, (Markov, 1971)

1. the next state of the system may depend only on the current state, and
2. all potential states of the system have to be realized in an infinite time,

thus resulting in a finite set where each state has at least one non-zero transition probability to another state, and whose future is conditionally independent of the past. While the state of such a system at a given time is generally unpredictable, its statistical properties may be known. This property makes the Markov chain a popular tool in applied mathematics.

A simple example of a Markov chain is a “random walk” among the integers from -10 to +10, starting from 0, with each step having an equal probability of being ± 1 . If the current state is either +4 or +6 at any time, the probability of the next state being +5 is 0.5, and 0 otherwise. Whether the state one step earlier was +3, +5 or +7 has no effect on the next state. In this example, the probability of states follows a normal distribution.

The Markov chain Monte Carlo (MCMC) methods randomly sample a probability distribution by using a Markov chain whose long-time equilibrium is that very same distribution (Metropolis et al., 1953). Although this may sound useless, there are many situations where the properties of a distribution may be too complex to be effectively studied by other means. While these are approximate in nature, the quality of the retrieved sample can be improved by increasing the number of samples. MCMC methods are used in e.g. physics, chemistry, mathematics, economics and social sciences for the purposes of statistics, optimization and numerical integration, and they are especially useful in problems with multiple dimensions.

A popular MCMC algorithm is the Metropolis–Hastings algorithm (Hastings, 1970), which can be implemented in the following way. Let the sampled probability distribution be $P(x)$. The algorithm then has to generate a Markov chain, where each state x_{t+1} depends only on the previous one, x_t . If the transition probabilities are assumed symmetric, the probability of the proposal state x_p being “accepted” is

$$\rho(x_t \rightarrow x_p) = \min\left(\frac{P(x_p)}{P(x_t)}, 1\right). \quad (9)$$

In other words, the proposal state is accepted if its probability $P(x_p)$ is higher than the probability of the current state $P(x_t)$, or if the ratio $P(x_p)/P(x_t)$ is “statistically close enough.” If the state is accepted, the next state becomes $x_{t+1} = x_p$, and if not then $x_{t+1} = x_t$.

A graphical example of an MCMC method at work is presented in Figure 9. The black line displays the accepted steps that the algorithm has taken while trying to find the maximum of probability in a two-dimensional space, where the probability is set to follow the normal distribution according to

$$P(x, y) = \exp\left(-\frac{(x - 5)^2 + (y - 5)^2}{10}\right). \quad (10)$$

Starting from the origin (0,0), the algorithm quickly approaches and gets very close to the center point (5,5), but because of “a series of bad luck,” ends up quite far until around the point (8,2) again turns to the right direction. This kind of behavior is inherent to random methods, and can only be avoided in a statistical sense: the more time the algorithm spends around a specific point, the higher its likelihood. Of course, in order to draw any statistical conclusions from the example, one should run it for a lot more steps. Estimating an efficient number of required steps for a converged solution is, however, an unmet challenge (Cowles and Carlin, 1996). However, with optimization in mind, one could of course choose the “best guess” as the final answer. This way the temporal order of the steps is unimportant. An approach like this was utilized in **Paper VI**.

The example case presented in Figure 9 demonstrates also some other problems related to the MCMC methods. Firstly, the number of steps needed for convergence to the solution is affected by the step size: more small steps are required before the algorithm

gets close to the maximum, but on the other hand, with big steps one risks taking a big wrong step or constantly “overshooting” the maximum. Secondly, if there was a second (albeit lesser) local probability maximum, e.g. at the point (10,0), the algorithm might have continued to approach it instead of turning around the point (8,2). Especially with a very small step size getting “trapped” near the wrong local maximum is a problem that is easiest to resolve by statistics: more (separate) runs with differing initial conditions.

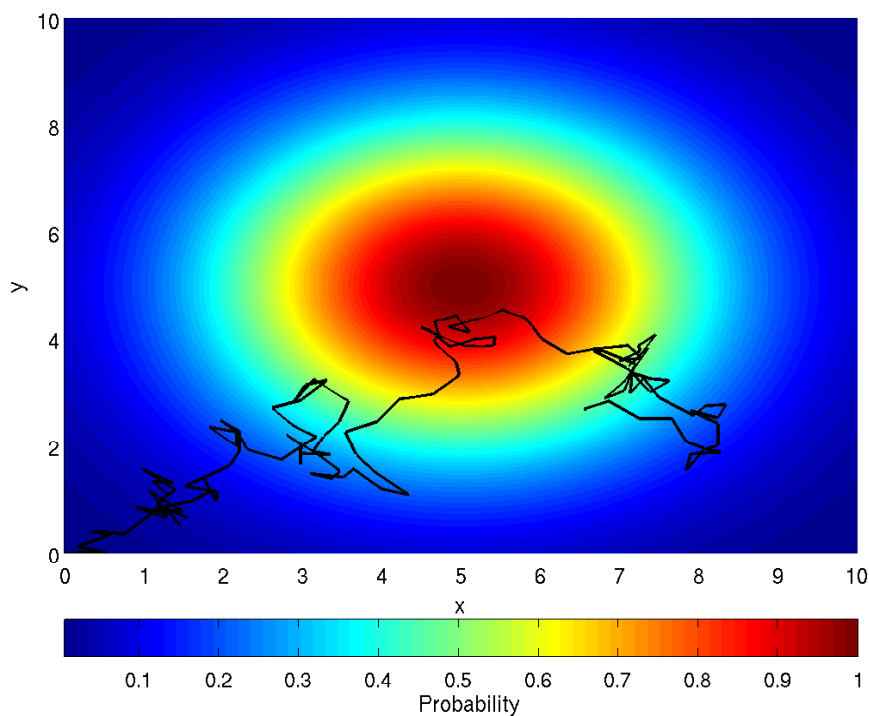


Figure 9: An example of a MCMC method trying to find the maximum of probability (distributed normally). Here, the method starts from the origin (0,0) and is given 150 steps to reach a solution. Only the accepted transitions are shown (black line).

The power of the MCMC methods lie in their easy implementation in various applications: since the requirements of Markov chains are easily met by model design, practically all that is needed is a sensible probability function. In **Paper VI**, the system states are represented by combinations of vapor concentrations, which link to the probability interpretation of modeled and measured difference in particle concentration. As a result, the algorithm is able to “predict” the ambient vapor concentrations needed to explain the observed particle growth.

6 Review of papers and the author's contribution

I alone am responsible for the introduction of this thesis.

Paper I investigates the connection between the sulphuric acid concentration and new particle formation by using the UHMA model. Special attention is given to the question of what could provide a linear dependence between $[\text{H}_2\text{SO}_4]$ and the concentration of 3–6 nm particles. It is concluded that the experimental findings are best met when a low-volatility organic vapor is present, and when the nucleation occurs via cluster activation closer to 2 nm than 1 nm. I performed some of the reported simulations and data analysis, and assisted in writing of the article.

Paper II presents semi-empirical parameterizations for several new nucleation mechanisms involving a low-volatility organic vapor. While no evident distinctions between particle concentrations from different mechanisms are found, the cluster activation schemes are suggested as more likely due to the higher correlation with reported field data with respect to the connection between the formation rate of 3 nm particles and the sulphuric acid concentration. A new, physically sound method is described for this 'fitting' that accounts for the varying time delay between the formation of a particle and its subsequent detection after growth to 3 nm. I performed the model simulations and data analysis reported in this study, developed the new fitting method and wrote almost all of the article.

Paper III investigates the relationship between different methods for calculating the formation rate of particles of certain size (3 nm in particular). The use of high-resolution model data enables a detailed comparison, and indicates some elemental differences between the approaches. The paper introduces an improved formula for the calculation of the formation rate. Additionally, the article investigates the temporal connection between the formation rate and the concentration of gaseous sulphuric acid by applying the method developed in **Paper II**, and concludes that the interpretation of the often implied power-law is inaccurate. I performed all the required simulations, data analysis, most of the calculations, found the introduced improvement in analysis and wrote a major part of the article.

Paper IV aims at providing global climate models with a simple iodine dioxide nucleation scheme. The paper reports parameterizations for nucleation involving OIO that have been derived from experimentally observed new particle formation events in

coastal environments. Ranges for nucleation coefficients and required production rates for the iodine dioxides are presented, along with sensitivity studies on various factors. The parameterization is applied in a remote marine scenario, and it is concluded that CCN production is feasible in the presence of additional vapors that assist in particular growth. I am responsible for the modified UHMA model, performed the simulations and data analysis, and wrote most of the paper.

Paper V studies the growth rates of particles observed at the Mace Head atmospheric research station in Western Ireland and onboard a research vessel. Experimental evidence for the link between particle size and age (i.e. the distance from measurement station) is found, and further tested in model calculations with the parametrization from IV. The first observations of purely open ocean new particle formation are also reported. For this study, I performed the model simulations, some data analysis and wrote a small part of the paper.

Paper VI introduces a powerful tool for data analysts and modelers, significantly reducing the amount of manual labor required to determine e.g. particle growth rates. The paper describes an algorithm that applies a Markov chain Monte Carlo method and an aerosol dynamics model to estimate what kind of combination of condensing vapors would yield a particle size distribution similar to an observed one. The MECCO algorithm displays excellent performance when using clean model data, and initial testing suggests reasonable results with experimental data as well. I had the original idea for the new algorithm, programmed an implementation of it and wrote almost all of the article.

7 Conclusions

One of the foci of this work has been the formation rate of new particles. This important quantity provides information on the nucleation mechanism and the vapors responsible for the formation of new particles, and on the other hand, their initial growth and related processes, such as coagulation. Because experimental observations have suggested that the formation rate of 3 nm particles closely resembles the sulphuric acid concentration raised to the power of 1–2 (Weber et al., 1996; Sihto et al., 2006; Riipinen et al., 2007; Kuang et al., 2008; Paasonen et al., 2010), potential explanations for this have been given, most notably the concepts of sulphuric acid induced activation of pre-existing clusters (Kulmala et al., 2006), and kinetic collision of two clusters containing a sulphuric acid molecule (McMurry and Friedlander, 1979). Model studies including **Papers I and II** have suggested that besides the nucleation mechanism, the mentioned exponent can be affected by various other conditions affecting the growth of the freshly formed particles, such as the assumed size of the critical cluster in the analysis.

Because the diurnal behavior of the sulphuric acid concentration is largely due to oxidation and the related photochemical activity, the general characteristics of this temporal behavior can be assumed for certain low-volatility organic vapors as well. This would help to explain the observations of many studies that have noted an organic component present in new particle formation (O’Dowd et al., 2002a; Bonn et al., 2008; Smith et al., 2008; Paasonen et al., 2009). The idea of an organic vapor participating in the nucleation and initial growth of new particles was modeled in **Paper II**, and it was found that the difference in the apparent formation rate at 3 nm was small, suggesting that the reports of sulphuric acid dependence could have also indicated dependence on the low-volatility organic vapor.

New particle formation in the marine environment has remained, with the exception of coastal regions, a little-studied area in aerosol science, the obvious reasons being expensive and difficult measurement conditions. Nevertheless, over 70% of the Earth is covered by water, and if the oceans turned out to be strong sources for particles, especially cloud condensation nuclei, these particles would have an important climatic effect. As was found in **Paper IV**, the estimated yields of oceanic precursor vapors are enough to form particles, and **Paper V** reported first measurements of purely open ocean new particle formation. However, their growth to CCN would require additional

condensing vapors, likely of organic origin.

The verification of many of these conclusions awaits the instrumental capabilities of accurate measurements of the condensing organic vapors and their properties. Meanwhile we have to rely on information gained via the growth rate analysis method described in e.g. **Paper II**. An interesting alternative is to apply advanced computer algorithms, such as the one developed in **Paper VI**. In the future, adaptive and self-learning analysis methods based on more advanced statistics may turn out to be extremely valuable.

In summary, the main conclusions and achievements of this thesis are the following, with emphasis on the contribution of yours truly:

1. experimentally observed new particle formation in boreal forest, coastal and marine environments was replicated in model studies
2. several first and second order nucleation mechanisms involving sulphuric acid, a low-volatility organic and iodine dioxide were parameterized, and the activation scenarios display best agreement with experimental observations
3. a more accurate method to study the dependence between the formation rate and the sulphuric acid concentration revealed likely dependencies on other factors, such as the concentration of low-volatility organics
4. the method used to determine particle formation rate from field data was investigated in detail, and improved
5. initial testing of a new method to estimate concentrations of condensing organic vapors showed promising results

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