# On the existence of neutral atmospheric clusters

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A recent hypothesis on the existence of neutral thermodynamically stable clusters is thoroughly investigated both experimentally and theoretically. Altogether, three different methods are utilized. First, the concentrations and size distributions of atmospheric ions, measured using ion spectrometers, are analyzed in parallel with aerosol size distribution data to find out the size dependencies of cluster and aerosol growth rates. The measurements are performed at SMEAR II station in Hyytiälä, Finland. Second, a condensation particle counter (CPC) is used as a nucleation chamber for homogeneous nucleation and ambient cluster activation studies. Both experimental methods support the existence of neutral clusters. Third, a large number of model simulations on aerosol and ion size distribution dynamics reveal that the existence of neutral clusters seems to be necessary to obtain consistency between modeling results and experimental measurements.

#### Introduction

Aerosol particles are ubiquitous in the Earth's atmosphere and influence the quality of our life in many different ways via their climatic and health effects, visibility, etc. Aerosol–cloud interactions are the most uncertain processes in predicting the climate change. The importance of atmospheric aerosols to the global radiation balance, cloud formation and human health has recently motivated several studies on aerosol formation. Bursts of particle formation have been observed in several regions around the world (Kulmala *et al.* 2004a), including the free troposphere (Clarke 1992, Raes *et al.* 1997, Schröder and Ström 1997, Weber *et al.* 1992, Hoppel *et al.* 1994,

Weber *et al.* 1998), coastal sites (O'Dowd *et al.* 1999), vicinity of evaporating clouds (Hegg *et al.* 1991, Clarke *et al.* 1998, Twohy *et al.* 2002), Arctic areas (Wiedensohler *et al.* 1996), urban areas (Mönkkönen *et al.* 2005), stack plumes (Kerminen and Wexler 1996) and boreal forests (Mäkelä *et al.* 1997, Kulmala *et al.* 2001).

From a theoretical point of view several nucleation mechanisms have been proposed to explain this particle production, such as ioninduced (or ion-mediated nucleation) (Yu and Turco 2001, Lovejoy *et al.* 2004) and ternary nucleation (Korhonen *et al.* 1999, Kulmala *et al.* 2000) along with meteorological-related nucleation enhancement processes such as turbulent fluctuations, waves and mixing (Easter and Peters 1994, Nilsson and Kulmala 1998). In coastal aerosol formation there likely is a significant contribution by iodide compounds (O'Dowd *et al.* 2002).

Recently it has been suggested that the formation of new aerosol particles is connected with the existence of atmospheric clusters (Kulmala et al. 2000). The existence of small ion clusters in the atmosphere has already been known for several decades (see e.g. Hörrak et al. 1998). The existence of neutral atmospheric clusters, however, has been an open question. This is due to the fact that we are still unable to measure these clusters directly. In this paper we investigate experimentally the existence of neutral clusters using condensation particle counters in a unique way. Furthermore, ion spectrometer data as well as ion and aerosol dynamic modeling are used to study the existence in both modeling and observational point of view.

In previous scientific literature there have been several hints about the existence of neutral clusters. In their measurements of pre-nucleation molecular clusters in a ternary NH<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O system Hanson and Eisele (2002) observed significant numbers of neutral clusters using a transverse chemical ionization apparatus. The composition of those clusters is likely to be similar to the atmospheric clusters observed in the present study. In the laboratory study by Kim et al. (1998), homogeneous and ion-induced nucleation were studied in the ternary NH<sub>3</sub>-SO<sub>2</sub>-H<sub>2</sub>O-air mixture. As a result of the study they proposed that the main mechanism is homogeneous nucleation of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> molecules produced by the H<sub>2</sub>SO<sub>4</sub>-NH<sub>3</sub> reaction. In any case the ammonium bisulphate clusters as well as multimers of them are the proper candidates for atmospheric neutral clusters (see also Vehkamäki et al. 2004).

## Hypothesis

A few years ago the following hypothesis, which in principle enables us to explain observed particle production bursts in the atmosphere, was suggested (Kulmala *et al.* 2000):

1. In the atmosphere, nucleation is occurring almost everywhere at least in daytime. The

conditions in the free troposphere (lower temperature, less pre-existing aerosols) are even more favourable for nucleation.

- Nucleation is maintaining a reservoir of thermodynamically stable clusters (TSC) which are too small to be detected by conventional instrumentation.
- Under certain conditions TSCs grow to detectable sizes (new particle formation) and further to CCN.

The TSCs can be ion clusters or neutral clusters. In atmospheric conditions, the main remaining open question is (Kulmala 2003): Do neutral, stable clusters generally exist, as indicated by aerosol dynamic model studies? Ion clusters certainly do (see Results and discussion below, and also Hörrak et al. 1998, and Arnold 1980). On the other hand it is straightforward to predict that neutral clusters will exist in the case of new particle formation via homogeneous nucleation (newly formed stable clusters are neutral) or even via ion-induced nucleation (ion recombination produces neutral clusters). However, now we try to find out if they could also exist although no new particle formation (to the measurable range of above 3 nm in diameter) is observed. Moreover, the ion-mediated particle formation (Yu and Turco 2001, Lovejoy et al. 2004) mechanism is able to predict rather similar formation rates as the ternary nucleation model. However, the nucleation rate predicted by the ion-mediated mechanism is limited by the ion production rate, which often gives smaller particle formation rates than observed (see Kulmala et al. 2004a) when the cluster sink due to scavenging by existing aerosols is taken into account. In this paper we present (i) experimental, (ii) observational and (iii) modeling results indicating the existence of neutral cluster in the atmosphere.

#### **Results and discussion**

A typical example of atmospheric particle formation and subsequent growth is shown in Fig. 1. The size spectra were measured using an Air Ion Spectrometer (AIS). The existence of ion clusters around 1 nm is clearly seen, and their concentration is relatively constant. The burst of new par-



**Fig. 1**. Typical aerosol formation and subsequent growth event measured using an ion spectrometer at SMEAR II station, Hyytiälä, Finland. *x*-axis is time of day and *y*-axis is the particle (ion) size. The balk indicates the concentration of each size ( $d(\text{ions})/d\log D$ ). The formation of new particles starts after 10:00. The subsequent growth continues during the day and particles reach size of 50 nm. The growth can be estimated to be around 4 nm h<sup>-1</sup>. The growth pattern supports ternary nucleation and subsequent growth by organic compounds. Note that the ion measurements extend to 0.5 nm, whereas the typical aerosol size distribution measurements start at 3 nm.

ticles (exceeding 1.5 nm in diameter) after 09:30 and their subsequent growth will significantly enhance the particle concentration in the size range > 3 nm. Using ion and aerosol size spectra together, the growth rate of aerosol particles as a function of their size can be determined. After investigation of more than 20 particle formation events, an increase in growth rate as a function of the particle size can be seen (Table 1). The observed growth rate is consistent with a cluster activation theory developed recently (Anttila et al. 2004, Kulmala et al. 2004b), but in conflict with the ion-mediated particle formation theory (Yu and Turco 2001). The ion-mediated particle formation theory predicts that the growth will decrease with increasing particle size (see also Kulmala et al. 2004c). Therefore, our finding supports the existence of neutral clusters.

A recently developed condensation particle counter (CPC UF-02, Lithuanian Institute of Physics and University of Helsinki) has been used to experimentally find out the existence of neutral clusters. The calibration of the CPC as well as the determination of the detection efficiency and losses within both the instrument and the tubing were conducted using the procedure described by Aalto *et al.* (2001) and Hämeri *et al.* (2002). Our measurements are based on: first, using the CPC as a nucleation chamber, and second, measuring the ambient aerosol concentration. These measurements were performed in the urban background of Helsinki in moderately-polluted air. In the first case the aerosol particles and ions were filtered out from the air entering the CPC, after which the temperature

**Table 1**. Mean growth rate as a function of size. The values are obtained by estimating the growth rate for all the event days during a measurement campaign at SMEAR II station (Finland, March–April 2003), and by averaging within three size ranges. The AIS is Air Ion Spectrometer, BSMA is Balanced Scanning Mobility Analyzer and DMPS is Differential Mobility Particle Sizer (for more details *see* Kulmala *et al.* 2004c).

Size range (nm)	Growth rate (nm h <sup>-1</sup> )	Devices
1.3–3	1.1	AIS, BSMA
3–7	2.9	AIS, BSMA, DMPS
7–20	5.5	AIS, DMPS



Fig. 2. Particle number concentration in the condensation particle counter as a function of the temperature difference between the saturator and the condenser. Both particle free air (black line) and ambient air with pre-existing particles (open symbols) are presented.

difference between the saturator and condenser and, consequently, the saturation ratio of butanol vapor were increased. At the temperature difference of 34 K or more, new particles were born in the CPC (Fig. 2). Thereafter, the normal atmospheric air with atmospheric aerosol particles was investigated. In this case, the pre-existing aerosol particles activate first. When saturation was further increased, smaller and smaller particles activated. At a certain point also TSCs started to activate. However, we should keep in mind that when ions and aerosol particles are filtered out, also a fraction of nucleating vapors could be filtered out. In that case the probabilities on cluster activation as well as on homogenous nucleation would be somewhat reduced, but the overall effect on the results is estimated to be small as compared with other uncertainties.

As the temperature difference was increased, the observed number concentration started to increase as new particles were formed. An estimation of the cluster concentration could be obtained by comparing these increases with and without pre-existing particles. The former case represents particle formation inside the CPC by homogeneous nucleation, while in the latter case also undetectable clusters were activated to form aerosol particles. We can see from Fig. 2 that the increase was larger with the preexisting particles, which means that all newly formed particles could not have been formed by homogeneous nucleation, i.e., they were the result of activated clusters. From the difference the number concentration of clusters may be estimated to be in the range 1000-10 000 cm<sup>-3</sup> (Fig. 3). The detection efficiency of the CPC in these sizes (1-3 nm) is only about 5%-30% due to diffusion losses, based on which we can estimate that the concentration of clusters was in the range 3000–200 000 cm<sup>-3</sup>. Accordingly, the ion cluster concentration can be estimated to have been at the maximum around 1000-2000 cm<sup>-3</sup> (see e.g. Hörrak et al. 1998, Laakso et al. 2004). Therefore, it seems that there should have been a significant number of neutral clusters in the atmosphere. Furthermore, this number is consistent with the original prediction (Kulmala et al. 2000). The air used in the experiment was urban air in Helsinki. Since we can observe neutral clusters already in moderately polluted air, it is likely that we can observe them in other air masses as well. We must note, however, that our instrument is still in a developmental stage and needs to be calibrated with more established models. Thus, these experimental findings should be regarded as somewhat preliminary.

A third way to investigate the existence of neutral clusters is aerosol and ion dynamic mod-





eling. The recently developed model AEROION (Laakso *et al.* 2002) has been further developed in order to be able to study the existence of neutral clusters. The model includes both ion-induced and ternary  $H_2SO_4-NH_3-H_2O$  nucleation mechanisms. The ternary mechanism can be used, and was used in our simulations, in barrierless (kinetic) form when actually only the sulphuric acid concentration affects the nucleation rate. The model also includes coagulation and condensation of sulphuric acid and arbitrary organic vapor. The organic vapor condensation is assumed to follow the parameterized version of cluster activation theory (Kerminen *et al.* 2004).

Although sulphuric acid is a key molecule for nucleation, its typical atmospheric concentrations are too small to explain the subsequent growth (Kulmala *et al.* 2004a). For this reason other condensable vapors are needed. In the model studies presented here, the organic vapour concentration was taken from the growth rate analysis carried out for the QUEST-campaign (Kulmala *et al.* 2004c). Other parameters taken from the measurements included particle size distributions in the size range > 40 nm, ion production rate, relative humidity, temperature, gaseous sulphuric acid concentration and average cluster ion properties for the calculations of ion-aerosol attachment coefficients (Laakso *et al.* 2004). In principle, the growth of neutral clusters to detectable sizes (> 3 nm in diameter) can be explained in two different ways. First, if the concentration of pre-existing aerosol particles is low due to precipitation or some other reason, the cluster self-coagulation may become significant (Kulmala *et al.* 2000). Second, if there is a large source of available condensable vapours (such as organics, inorganic acids and ammonia) the cluster growth by condensation to detectable sizes and even to the Aitken mode takes place in only a few hours.

A large number of model runs were performed using the sectional aerosol and ion dynamic model AEROION under the observed atmospheric conditions. The model results were compared with several experimental results, particularly those measured in spring 2003 at the SMEAR II station in Hyytiälä, Finland (Figs. 4 and 5). One can see that the model results agree with the observed ones not only qualitatively but also reasonably well quantitatively. The model was able to reconstruct the small ion concentration, ion mobility distribution, particle number size distributions and even the ratio between negative and positive ions as a function of size and time (see Laakso et al. 2004 for more details). The effect of pre-existing particles was also visible: if the concentration was low (25.3.2003),



**Fig. 4.** Modeled concentrations of ions and aerosol particles. In the upper picture the total (neutral + charged) concentration of particles > 3 nm and of cluster ions (0–1.5 nm) is shown. Lower picture shows the concentration of ions in size-ranges 1.5–3 and 3–5 nm and the concentration of particles between 3 and 5 nm. In addition, the calculated concentration of TSCs (neutral clusters between 1 and 3 nm) is shown as a thick, solid curve.

particles were observed in sizes > 3 nm, but if the concentration was larger (27.III.2003), scavenging prevented the particle growth even if there were enough organic vapors. Furthermore, the model results suggest the existence of a significant number of neutral clusters (Fig. 4). The most probable mechanism for new particle formation was found to be kinetic nucleation seasoned with a slight contribution of cluster ion growth. TSCs were also found to be a possible explanation to the stable cluster ion concentrations during the particle formation bursts.

### Conclusions

In this paper both experimental and theoretical support is given for the existence of neutral clusters in the atmosphere. In order to be able to study the thermodynamically stable cluster hypothesis (Kulmala *et al.* 2000), we utilized three recently developed methods. First, we used ion spectrometer data together with aerosol size distribution data to find out the size dependencies of cluster and aerosol growth rates. Second, we used a CPC as a nucleation chamber for homogeneous nucleation and ambient cluster activation studies. Third, aerosol model calculations revealed that the existence of neutral clusters is needed to obtain consistent modeling results with experimental measurements.

Our usage of the new CPC as a cluster activation chamber is not the only experimental setup where neutral clusters can be or even have been observed. Gamero-Castaño and de la Mora (2000) proposed clusters as "impurities in the gas phase". However, their study focused on the activation of ions and charged nanoclusters.



**Fig. 5**. Observed concentration of sulphuric acid, ions and aerosol particles. In the upper picture the total (neutral + charged) concentration of particles > 3 nm and the concentration of cluster ions (0-1.5 nm) is shown. The lower picture shows the concentration of ions in size-ranges 1.5–3 and 3–5 nm and the concentration of particles between 3 and 5 nm.

Some hints on this topic were already observed by Sgro and de la Mora (2004) under laboratory conditions. However, so far the proper explanation has been missing. The best hint on the existence of neutral clusters so far is the observations by Weber *et al.* (1995). They observed clusters — probably neutral — during the new particle formation burst at Mauna Loa in 1992 using a mass spectrometer. Their results also show that neutral clusters may exist, even if the new particle formation (> 3 nm) is negligible.

The model studies conducted were "trial and error" in nature. Several (combinations of) nucleation mechanisms as well as size dependencies of the growth rate on particle size were used. The best results were obtained by using a barrierless (kinetic) ternary nucleation mechanism together with a size dependent growth rate, supporting the recently suggested nano-Köhler theory (Kulmala *et al.* 2004b). The model not only was able to predict the existence of nucleation events, but also with reasonable accuracy the concentrations of both neutral and charged particles of all sizes.

Globally, the formation of new particles and their subsequent growth seems to take place almost everywhere (Kulmala et al. 2004a). Ion clusters are always present (see Fig. 1) and here we have given evidence that also neutral clusters exist, and probably are always present in daytime. However, more precise laboratory experiments and observations in different environments are still needed. The formation of new aerosol particles (to measurable sizes) seems to be controlled by the very initial steps of the growth of the clusters and condensation/coagulation competition. The new particle production can, depending on the location, increase the concentration of cloud condensation nuclei by a factor of more than two over the course of one day (Kulmala 2003). We can therefore conclude Acknowledgements: We would like to thank financial support by The Academy of Finland, and Prof. H. Tammett, Dr. U. Hörrak and Dr. M. Vana for informative discussions concerning the ion spectrometer data.

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