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On the concept of condensation sink diameter

Kari E. J. Lehtinen, Hannele Korhonen, Miikka Dal Maso and Markku Kulmala

Department of Physical Sciences, P.O. Box 64, FIN-00014 University of Helsinki, Finland

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The condensation sink has turned out to be a useful concept in the evaluation of atmospheric aerosol dynamics. Particularly, using growth rates together with the condensation sink will help understanding the formation and growth processes of atmospheric aerosols. In this paper, we develop this formalism even further and introduce the concept of condensation sink diameter (CSD). It can be successfully used both when analyzing experimental data as well as in model calculations, especially when using simple multimodal monodisperse methods. The observed values of CSD for the whole distribution in Hyytiälä are seen to be of the order 100 nm. The connection between number median diameter, surface area diameter and CSD is investigated in depth as well as the role of the CSD when designing model runs of atmospheric particle formation and growth.

Introduction

Aerosol particles have a significant role in different technical and environmental applications. In spite of their triggering role in the atmosphere, they are important e.g. for producing new nanomaterials, in understanding nuclear power plant accidents, and combustion. Atmospheric aerosols are ubiquitous in the Earth's atmosphere and affect our quality of life through many different processes. In polluted urban environments, aerosol emissions can affect public health through inhalation (Donaldson *et al*. 1998), whilst regionally and even globally aerosols are thought to contribute to climate change patterns (Charlson *et al*. 1987). In recent years, considerable effort has been devoted to understanding how aerosols directly affect the Earth's radiation budget through direct backscatter of incoming solar radiation, thus contributing to a planetary cooling. Not only do aerosols directly affect the radiation budget, they also contribute to this budget indirectly through the formation of cloud droplets and clouds. It is generally considered that an increase of aerosols will lead to brighter and more sustained cloud cover, thus providing additional planetary cooling.

In order to be able to understand the effects of atmospheric aerosols, their dynamics should be investigated in detail. The formation and growth of atmospheric aerosols are key processes in determining their dynamics. The formation of ultrafine particles detected at a few nm, and subsequent growth to ~100 nm in 1–2

days, has been observed frequently in the continental boundary layer. Such observations span from northern-most sub-arctic Lapland, over the remote boreal forest (Mäkelä *et al*. 1997, Kulmala *et al*. 1998, Kulmala *et al*. 2001a) and suburban Helsinki (Väkevä *et al*. 2000), to industrialised agricultural regions in Germany (Birmili and Wiedensohler 1998) and also to coastal environments around Europe (O'Dowd *et al*. 1999). The atmospheric new particle formation rates have also been investigated by Weber *et al*. (1996, 1997) and Kulmala *et al*. (2001b), and the biogenic aerosol formation by Kavouras *et al*. (1998).

In this study, we introduce the concept of the condensation sink diameter (CSD). The concept of the condensation sink itself has turned out to be useful in analysing the formation and growth processes of nucleation mode aerosols (Kulmala *et al*. 2001b, Kerminen and Kulmala 2002, Dal Maso *et al*. 2002). After the definition we compare it with other typical diameters, the number median diameter (NMD) and the diameter of mean surface area $\bar{d}_a$, related to the aerosol size distribution. Then we investigate its daily pattern in Hyytiälä (SMEAR II) station. Hyytiälä (61°51′N, 24°17′E) is in the Boreal forest region of central southern Finland. It is one of two sites for the Finnish SMEAR stations (Station for Measuring Forest Ecosystem–Atmospheric Relations) hosting continuous long-term monitoring of atmospheric processes such as turbulent fluxes and aerosol physico-chemical interactions. Finally, we show how the CSD concept can be used as a useful modelling tool, especially when setting up multimodal monodisperse simulations of particle formation and growth.

Condensation sink diameter

Condensation sink

The aerosol condensation sink determines how rapidly molecules will condense onto pre-existing aerosols and depends strongly on the shape of the size distribution (*see* e.g. Pirjola *et al*. 1999). As an example, let's look at the concentration of some condensable vapour C, which is determined by its source, nucleation and condensation, can be expressed by

$$\frac{dC}{dt} = Q - Jn^* - \mathrm{CS} \times C, \tag{1}$$

where Q is the source rate, J the nucleation rate and n^* is the number of condensable vapour molecules in the critical cluster. Here, the evaporative flux from the particles was assumed negligible. The condensation sink CS, with unit s^{-1}, describes the loss rate of molecules with diameter d_p, diffusion coefficient D and mean free path λ_v onto a distribution $n(d_p)$ (or N_i in the discrete case) of existing particles and, thus, is obtained by integrating (or summing) over the size spectrum:

$$\begin{aligned} \mathrm{CS} &= 2\pi D \int_0^\infty d_p \beta_M(d_p) n(d_p) dd_p \\ &= 2\pi D \sum_i \beta_{M_i} d_{p,i} N_i \,. \end{aligned} \tag{2}$$

The transitional correction factor β_M can be expressed as (Fuchs and Sutugin 1971)

$$\beta_M = \frac{\mathrm{Kn}+1}{0.377\mathrm{Kn}+1+\frac{4}{3}\alpha^{-1}\mathrm{Kn}^2+\frac{4}{3}\alpha^{-1}\mathrm{Kn}} \tag{3}$$

with Knudsen number $\mathrm{Kn} = 2\lambda_v/d_p$ and mass accommodation coefficient α. In the molecular regime where $\mathrm{Kn} >> 1$ we have

$$\beta_M \xrightarrow[d_p \to 0]{} \frac{3d_p}{8\lambda_v} \tag{4a}$$

and

$$\mathrm{CS_d} \propto d_p^2. \tag{4b}$$

In this case, $\mathrm{CS_d}$ denotes the condensation sink caused by a monodisperse population of particles of diameter d_p. On the other hand in the continuum regime where $\mathrm{Kn} << 1$ we get

$$\beta_M \xrightarrow[d_p \to \infty]{} 1 \tag{5a}$$

and

$$\mathrm{CS_d} \propto d_p. \tag{5b}$$

Typically the tropospheric aerosol, however, also consists of particles occupying the transitional regime. In this case, at least locally, we can write $\mathrm{CS_d} \propto d_p^a$ where $1 < a < 2$. The actual local, size dependent, value for the growth expo-

nent a can be obtained by differentiation:

$$a(d_p) = \frac{d(\ln \mathrm{CS}_d)}{d(\ln d_p)} = \frac{1}{\mathrm{CS}_d} \times \frac{\mathrm{Kn} + \left(0.754 + \frac{8}{3\alpha}\right)\mathrm{Kn}^2 + \left(0.377 + \frac{16}{3\alpha}\right)\mathrm{Kn}^3 + \frac{8}{3\alpha}\mathrm{Kn}^4}{\left[\mathrm{Kn} + \left(0.377 + \frac{4}{3\alpha}\right)\mathrm{Kn}^2 + \frac{4}{3\alpha}\mathrm{Kn}^3\right]^2} \quad (6)$$

In accordance with Eqs. 4 and 5 above, the exponent approaches the value 2 for small particle sizes (*see* Fig. 1), corresponding to condensation rate being proportional to particle surface area. With increasing particle size, the value smoothly drops, approaching the value 1 in the continuum size regime. In this regime, the condensation rate is proportional to particle diameter.

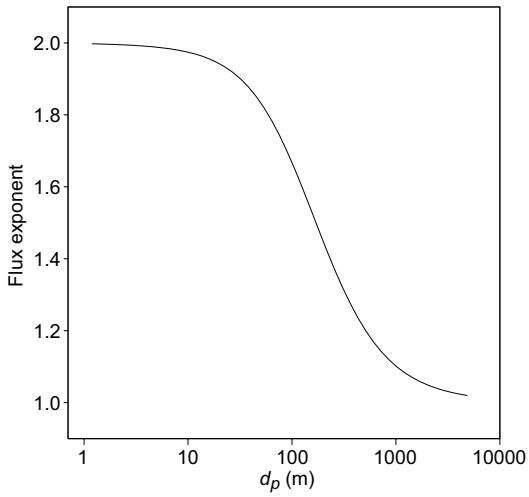

Fig. 1. The exponent in the condensational growth rate according to Eq. 6, as a function of particle size, when the growth rate is assumed locally to be of power-law form.

CSD

The condensation sink diameter, CSD, of a distribution of particles with total number concentration N_{tot}, is the diameter where a monodisperse population of particles of number concentration N_{tot} should be placed to obtain the same total condensation sink CS as for the polydisperse distribution of interest. In mathematical form its definition is therefore:

$$2\pi \times D \times \mathrm{CSD} \times \beta_M(\mathrm{CSD}) \times N_{tot} = 2\pi \times D \sum_i \beta_{M_i} d_{p,i} N_i = \mathrm{CS}. \quad (7)$$

To illustrate how the CSD depends on the particle size distribution we calculated it for several lognormal distributions of different locations (1 nm < NMD < 10 000 nm) and width ($1.4 < \sigma_g < 2.0$), where NMD = Number Median Diameter and σ_g = geometric standard deviation (Fig. 2). Since the condensation sink is proportional to the surface area in the free molecular regime, it is obvious that the CSD should approach the diameter of mean area $d_{a,ave}$ of the distribution, as clearly is the case. Furthermore, since the condensation sink is proportional to particle diameter in the continuum regime, the CSD should approach the number mean diameter d_{ave}. Thus, if the total surface area of the distribution is presented as an indicator of condensational vapour sink, as many times is the case, the deductions may not be worth much for a distribution with a large tail stretching into the continuum regime.

Another important result clearly shown in Fig. 2 is that deviations between different characteristic diameters increase with increasing σ_g. For example, in the free molecular regime for a lognormal distribution with σ_g = 2.0 the CSD is 1.62 times larger than the NMD but only 1.33 times larger for σ_g = 1.7. This means that if particle dynamics is to be simulated, approximating the location of particle modes with their number median diameter, which intuitively may be the first natural choice, results in serious error when dealing with condensation dominated processes. These effects on modelling will be further discussed in the modelling chapter.

Aerosol size-distribution measurements

As an example of the size dependence of the condensation sink (CS) for a measured distribution we show it in $d(\mathrm{CS})/d(\log d_p)$-form for 9 January 1999 at 19:49 measured at Hyytiälä station in Fig. 3. It is compared with the number size distribution as well as the surface area distribution. The total number concentrations and size

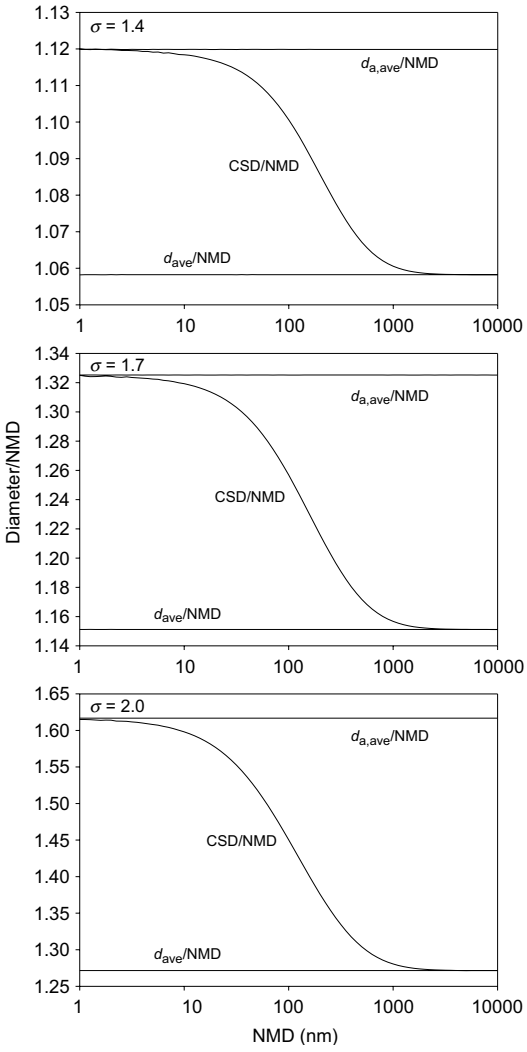

Fig. 2. The condensational sink diameter (CSD) for lognormal distributions of different location (number median diameter NMD) and width (geometric standard deviation σ) compared with number mean diameter d_{ave} and diameter of mean surface $d_{a,ave}$, all normalised by NMD.

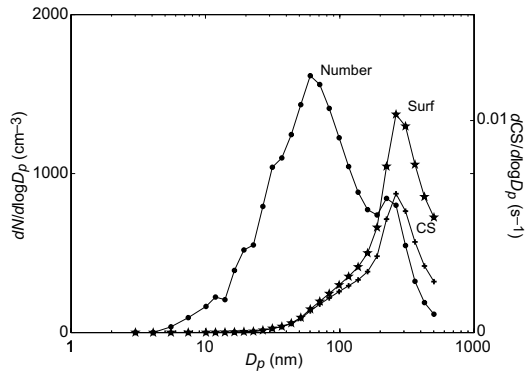

Fig. 3. Number distribution, Surface area distribution and condensation sink (CS) distribution as a function of particle size, measured at Hyytiälä station in Finland on 9 Jan. 1999 at 19:49. The peak value of the surface distribution is 5.14×10^{-11} m^2 cm^{-3}.

distributions were measured using well-known CPC and DMPS techniques (*see* details in Aalto *et al*. 2001). As seen in the figure, the dominating Aitken mode of the number distribution plays a minor role in term of the condensation sink. The major part of the CS comes from the accumulation mode, centered at about 250 nm. This is also why the surface area is not a very good measure in many cases when dealing with condensational growth. As the major portion of the CS can be attributed to the larger accumulation mode particles the size dependence of the CS approaches d_p instead of d_p^2.

Daily patterns of the CSD, again measured at Hyytiälä station on 16 March 2000 (nucleation event day) and 9 January 1999 (non-event day) as a function of time are shown in Fig. 4. The CSDs are shown for the modes separately, as well as for the entire distribution. The NMDs of the modes are also shown in the plots. On the event day the CSD varies in the range 50–80 nm, whereas for the non-event day it is 100–200 nm. It is yet unclear if this is a general trend that event days exhibit a smaller value for the CSD than non-event days. This issue will be looked upon in more detail in the near future. Another interesting feature of the figures, again, is that the CSD and NMD for the modes may deviate quite significantly. Thus it is important to pay attention to the choice of characteristic diameter when choosing model parameters. The next chapter will deal with this aspect in some more detail.

Modelling

One instance where the concept of condensational sink diameter is of tremendous use is monodisperse modelling. A multimodal monodisperse method may be a good choice e.g. in combination with a larger scale atmospheric 3D model in which not much weight can be put into

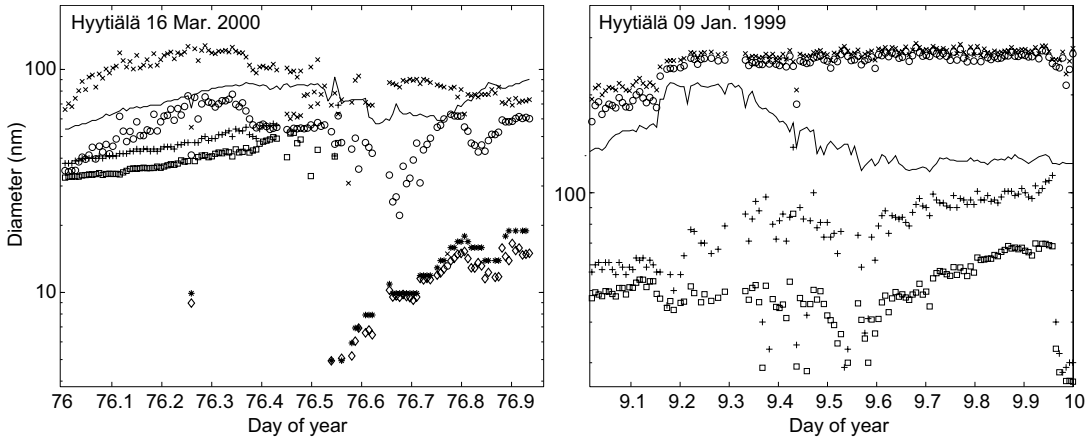

Fig. 4. Evolution of CSD for accumulation mode (x), Aitken mode (+) and nucleation mode (★) as well as whole distribution (solid line) and NMD for accumulation mode (o), Aitken mode (□) and nucleation mode (◆). The plots are for a nucleation event day (16 Mar. 2000) and a non-event day (9 Jan. 1999).

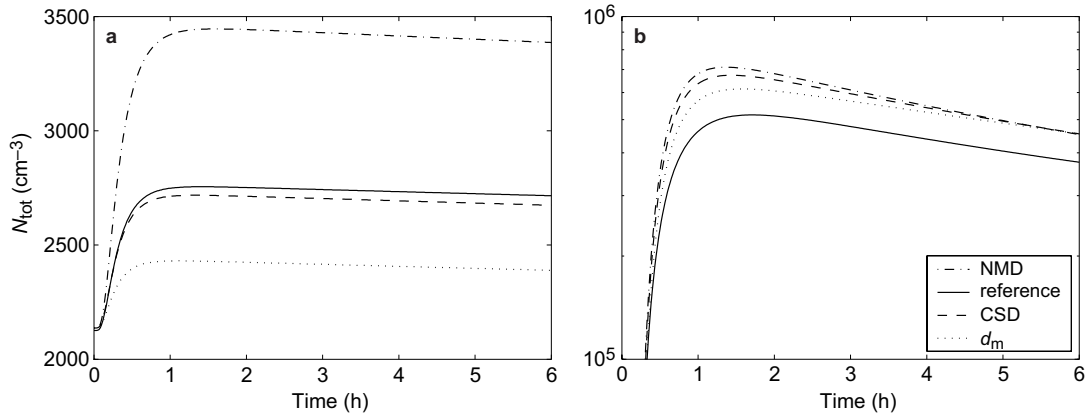

Fig. 5. Evolution of the total number concentration in a nucleation event for rural (**a**) and marine (**b**) conditions (*see* detailed conditions in text). Simulation was executed using a multimodal monodisperse method with mode locations placed at different characteristic sizes: condensation sink diameter (CSD), number median diameter (NMD) and diameter of mean mass d_m. The reference result is that of a sectional model with 100 fixed sections.

the aerosol dynamics submodel. The question then is: how to choose the locations of the monodisperse modes?

To investigate this issue in detail, we simulated homogeneous particle formation simultaneously with other aerosol dynamics (coagulation, condensational growth) with a three-mode monodisperse model and compared the results to those obtained from a fixed sectional model with 100 size sections (denoted reference hereafter). This level of resolution in a fixed sectional model was shown by Korhonen *et al*. (2003) to reproduce the results of a discrete solution with very good accuracy in several simulations of the evolution of the size distribution in particle formation and growth events. In the monodisperse model, conservation of number concentration in each pre-existing mode left us with several intuitively reasonable ways to select the location of these modes. We compared three ways to set the location and placed the particles at the geometric number mean diameter, at the diameter of average mass, or at the condensation sink diameter of each respective mode.

We also investigated (*see* Fig. 5) the particle number concentration evolution obtained using the different approaches at typical rural and marine conditions (Seinfeld and Pandis

1998). At rural conditions (Fig. 5a), the pre-existing particle concentration was relatively high, around 2000 cm^{-3}. This emphasized the importance of the pre-existing particles acting as a condensation sink for nucleating vapour molecules and thus, depressing the nucleation rate. At such conditions, the best initial location for the monodisperse particle modes was clearly at the CSD. Placing each mode at the number median diameter (NMD) of the respective mode underestimated both the coagulational loss of newly formed particles and the amount of sulphuric acid condensing on pre-existing particles. Compared with the reference model, therefore, this approach predicted a higher total particle concentration. In contrast, when the initial diameter in the monodisperse model was determined by matching the total masses of the modes, i.e. placing the mode at the diameter of mean mass ($d_{\bar{m}}$), the underestimation of total particle concentration was due to reduced sulphuric acid concentration as the approach predicts too high a sink for the vapour.

In marine conditions (Fig. 5b), the low pre-existing particle concentration of around 100 cm^{-3} led to a high new particle formation rate. Then, although its overall performance was fairly good irrespective of the way to initialize the size locations, the multimodal monodisperse model could not account for all the coagulational scavenging of small nanometer sized particles. This resulted from the fact that although the monodisperse nucleation mode predicts well the average diameter of the reference model mode, it excludes the very smallest new particles. The smaller the particles, however, the faster their coagulational loss. In both model runs, particle production was assumed to be caused by ternary water — sulfuric acid — ammonia nucleation (Napari *et al.* 2002) at 285 K temperature and 50% relative humidity. The sulfuric acid source and ammonia mixing ratio were assumed constant, at 8300 cm^{-3} s^{-1} and 10 ppt, respectively.

Conclusions

In this study, the concept of condensation sink diameter (CSD) has been introduced. As shown earlier, the condensation sink itself has turned out to be useful in studying the formation and growth of atmospheric aerosols. This is mainly due to the fact that in atmospheric aerosol dynamics, in addition to nucleation, condensation is the key process, and the formation rate of new particles is closely related to condensation. Here, we look into the properties of the CSD for distributions of different location and form and make some preliminary analysis of its time behaviour for aerosols in Hyytiälä, Finland.

The method has been applied to two different cases measured in Hyytiälä, one being a day with an observed nucleation event the other with no event. On the event day, the CSD for the whole distribution varied in the range 50–80 nm and on the non-event day in the range 100–200 nm. If there is a trend that nucleation event days exhibit smaller values for the CSD than non-event days is yet unknown and will be one key issue of further studies.

The CSD is a useful tool when setting up model runs using multimodal monodisperse models. Example runs with typical rural and marine background aerosol were performed with a ternary water-sulfuric acid-ammonia particle production mechanism. Using the monodisperse model together with sectional and exact ones we have shown that CSD is the best diameter to use to estimate the proper size for existing particles, especially for condensational growth dominated cases.

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