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Dynamics of atmospheric nucleation mode particles: a timescale analysis

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ABSTRACT

A theoretical framework was constructed by which one can estimate the relative role of different processes in the dynamics of atmospheric nucleation mode particles. The framework relies on 14 timescales that describe (1) changes in the total nuclei number concentration, (2) changes in the mean diameter of the nucleation mode and (3) concentrations of low-volatile vapours responsible for the growth of nuclei. The magnitude of the derived timescales can be calculated relatively easily from the available measurement or modelling data. Application to the lower-troposphere revealed that under most conditions removal of nuclei is dominated by their coagulation with larger background particles and that this process competes very strongly with growth of nuclei to sizes relevant to atmospheric chemistry and physics. With some exceptions, self-coagulation of nuclei was shown to be of marginal importance compared with their growth by condensation and their removal by coagulation. Finally, by comparing predictions based on relevant timescales with those obtained from detailed numerical simulations, quantitative criteria were derived concerning (1) when one may neglect self-coagulation of nuclei when looking at nucleation mode dynamics and (2) when the whole nucleation mode can be neglected because of its eventual removal. These criteria are extremely useful for atmospheric modellers who need to simplify their models as much as possible. From the modelling point of view, other processes requiring further attention are the introduction of new nuclei into the system and decrease in nuclei number concentration due to dilution of the air.

1. Introduction

The smallest aerosol particles present in the atmosphere, including stable molecular clusters and detectable particles up to sizes of about 20–25 nm in diameter, are called collectively the nucleation mode. While probably too small to have any direct atmospheric significance, nucleation mode particles may grow in size and ultimately become part of the larger particle population. Therefore, the significance of a nucleation mode is tied to its dynamical evolution rather than its general properties in the atmosphere.

The time evolution of an atmospheric nucleation mode is dependent on several interacting processes, including the production of new nucleation mode particles (nuclei), their growth to larger sizes, their removal to various surfaces and their atmospheric transportation. The production of nuclei involves two entirely different routes. One of them is atmospheric formation from various precursor gases, which has been observed to take place in a number of different environments all over the world (Kulmala et al., 2004a, and references therein). The other route is direct emission of these particles, such as in vehicular emissions in urban environments (e.g. Zhu et al., 2002). Once in the atmosphere, the nuclei grow in size by condensation of gaseous vapours and by self-coagulation. The removal of nuclei takes place by coagulation and surface deposition. Atmospheric transportation moves nuclei from one place to another, reducing their concentration in areas with active production of nuclei and increasing it elsewhere.

Accurate simulation of all the processes affecting the nucleation mode requires a numerical model with a very high particle size resolution. Such models, while available (e.g. Lehtinen and Kulmala, 2003), cannot be used in atmospheric problems because of their huge computational demands. In practical applications nucleation mode dynamics is dealt with by parametrizing the processes affecting the nuclei number concentration and/or size (Zhang et al., 1999; Kerminen and Kulmala, 2002; Korhonen et al., 2003). This approach is subject to large uncertainties because of many simplifying assumptions and may totally fail under some atmospheric situations. Perhaps the best way to deal

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with the nucleation mode would be to use some sort of hybrid approach, in which the processes central to the dynamics are simulated as accurately as possible and less significant processes are neglected altogether. This requires knowing the relative importance of the processes involved—information that is not usually available *a priori*.

In the current work, we construct a theoretical framework by which one can estimate which processes affect the dynamics of a nucleation mode under different atmospheric conditions. The framework relies on characteristic timescales, the magnitude of which can be calculated relatively easily from available measurement or modelling data. The power of such timescales has been demonstrated earlier in analysing the processes associated with atmospheric liquid-phase chemistry (Schwartz, 1988; Shi and Seinfeld, 1991), aerosol dynamics in plumes (Kerminen and Wexler, 1995a) and aerosol particle growth processes (Kerminen and Wexler, 1995b). Timescales have also been used to find out which aerosol processes need to be included in urban air quality models (Wexler et al., 1994; Zhang and Wexler, 2002a). We start our investigation by deriving expressions for the relevant timescales involved, after which a brief analysis of their relative magnitude under different atmospheric conditions will be performed.

2. Theory

2.1. *Basic equations governing nucleation mode dynamics*

The minimum amount of information needed to describe a nucleation mode is its total particle number concentration, N_{nuc}, and its number mean diameter, d_{nuc}. In a Lagrangian air parcel, the time evolution of N_{nuc} is obtained from the following equation:

$$\begin{aligned}\frac{\mathrm{d}N_{\mathrm{nuc}}}{\mathrm{d}t} &= J_{\mathrm{nuc}} - \frac{1}{2}K(d_{\mathrm{nuc}}, d_{\mathrm{nuc}})N_{\mathrm{nuc}}^2 \\ &\quad - N_{\mathrm{nuc}}\sum_j K(d_{\mathrm{nuc}}, d_j)N_j \\ &\quad - \left.\frac{\mathrm{d}N_{\mathrm{nuc}}}{\mathrm{d}t}\right|_{\mathrm{dep}} - \left.\frac{\mathrm{d}N_{\mathrm{nuc}}}{\mathrm{d}t}\right|_{\mathrm{dil}} - \left.\frac{\mathrm{d}N_{\mathrm{nuc}}}{\mathrm{d}t}\right|_{\mathrm{out}},\end{aligned} \tag{1}$$

where J_{nuc} is the production rate of nuclei, $K(d_1, d_2)$ is the coagulation coefficient between particles of diameter d_1 and d_2, and N_j and d_j are the number concentration and mean diameter of particles in the size section j. The different terms on the right-hand side of eq. (1) represent changes in the nuclei number concentration due to their production, coagulation with other nuclei (self-coagulation), coagulation with larger particles, surface deposition, dilution of the air parcel and growth of particles out of the nucleation mode, respectively.

The mean diameter of the nucleation mode is affected by the growth of existing nuclei due to condensation and self-coagulation, and by the production of new nuclei:

$$\frac{\mathrm{d}d_{\mathrm{nuc}}}{\mathrm{d}t} = \frac{2I_m(d_{\mathrm{nuc}})}{\pi\rho_{\mathrm{nuc}}d_{\mathrm{nuc}}^2} - \frac{J_{\mathrm{nuc}}}{N_{\mathrm{nuc}}}\left(d_{\mathrm{nuc}} - d^*\right). \tag{2}$$

Here I_m is the net mass flux into a single nucleus, ρ_{nuc} is the density of nuclei and d^* is the diameter of the new nuclei introduced into the system. The mass flux I_m is a sum of two separate terms which are that due to condensation, $I_{m,\mathrm{cond}}$, and that due to self-coagulation, $I_{m,\mathrm{scoa}}$. The condensational mass flux may be written as

$$\begin{aligned}I_{m,\mathrm{cond}}(d_{\mathrm{nuc}}) &= 2\pi d_{\mathrm{nuc}}\sum_i \Big(D_i\beta(Kn_{\mathrm{nuc}}, \alpha_i) \\ &\qquad \times [C_i - C_{i,eq}(d_{\mathrm{nuc}})]\Big),\end{aligned} \tag{3}$$

where D_i is the diffusion coefficient of a vapour i, C_i is its mass concentration in the gas phase and $C_{i,\mathrm{eq}}$ is the respective equilibrium concentration over the surface of the nucleus. The term β is the non-continuum correction factor for condensation and is given by (Fuchs and Sutugin, 1971):

$$\beta(Kn, \alpha_i) = \frac{1 + Kn}{1 + 0.337Kn + 1.33Kn(1 + Kn)/\alpha_i}, \tag{4}$$

where Kn is the Knudsen number and α_i is the mass accommodation coefficient of the condensing vapour on the surfaces of the nuclei. In self-coagulation every collision destroys two existing nuclei and produces one slightly larger nucleus. Effectively, this corresponds to the following mass flux into a nucleus:

$$I_{m,\mathrm{scoa}}(d_{\mathrm{nuc}}) = \frac{1}{6}\pi d_{\mathrm{nuc}}^2\rho_{\mathrm{nuc}}K(d_{\mathrm{nuc}}, d_{\mathrm{nuc}})N_{\mathrm{nuc}}. \tag{5}$$

Note that eq. (5) is not valid for individual nuclei but represents a flux that has been averaged over all nuclei.

Only vapours having an extremely low saturation vapour pressure, such as sulfuric acid and some organic compounds, are able to grow small nucleation mode particles (e.g. Kerminen et al., 2000; Anttila and Kerminen, 2003). These kind of vapours are expected to condense practically irreversibly into larger pre-existing particles, so that their mass concentrations in the gas phase can be calculated from the equation:

$$\frac{\mathrm{d}C_i}{\mathrm{d}t} = m_iP_i - \mathrm{CS}\times C_i, \tag{6}$$

$$\mathrm{CS} = 2\pi D_i\sum_j d_j\beta(Kn_j, \alpha_i)N_j. \tag{7}$$

Here P_i is the rate of production of vapour due to chemical reactions, m_i is the mass of a single vapour molecule and CS is a so-called "condensation sink" (e.g. Kulmala et al., 2001b). CS is a measure of the rate by which the vapour condenses onto the whole particle population.

2.2. *Relevant timescales involved*

Based on the discussion presented earlier, it is clear that there are three different classes of timescale that determine the nucleation mode dynamics: (1) those associated with changes in the total nuclei number concentration, (2) those associated with changes in the mean diameter of nuclei and (3) those associated with concentrations of condensable vapour. The overall timescale over which the total nuclei number concentration changes, $(1/N_{\mathrm{nuc}} \times \mathrm{d}N_{\mathrm{nuc}}/\mathrm{d}t)^{-1}$, can be split into several individual timescales by dividing both sides of eq. (1) by N_{nuc} and by looking at the various terms in this equation. The first timescale is that for the production of nuclei given by

$$\tau_{\mathrm{prod}} = \frac{N_{\mathrm{nuc}}}{J_{\mathrm{nuc}}}. \tag{8}$$

Removal by self-coagulation occurs over a timescale

$$\tau_{\mathrm{R,scoa}} = \frac{2}{K(d_{\mathrm{nuc}}, d_{\mathrm{nuc}})N_{\mathrm{nuc}}} \tag{9}$$

and that by coagulation with larger particles over a timescale

$$\tau_{\mathrm{R,coag}} = \frac{1}{\sum_j K(d_{\mathrm{nuc}}, d_j)N_j} = \frac{1}{\mathrm{CoagS}(d_{\mathrm{nuc}})}. \tag{10}$$

Here the term CoagS is also known as the “coagulation sink” (Kulmala et al., 2001b). The timescale for removal by surface deposition is given by

$$\tau_{\mathrm{R,dep}} = \frac{h_{\mathrm{mix}}}{v_{\mathrm{d}}(d_{\mathrm{nuc}})}, \tag{11}$$

where $v_{\mathrm{d}}(d_{\mathrm{nuc}})$ is the nuclei deposition velocity and h_{mix} is the mixed layer height. A change in the nuclei number concentration due to dilution may involve the boundary layer growth (blg), detrainment into the free troposphere (det) and, in the case of a plume, turbulent diffusion (dif). The relevant timescales for these three processes are given by

$$\tau_{\mathrm{dil,blg}} = \left(\frac{1}{h_{\mathrm{mix}}}\frac{\mathrm{d}h_{\mathrm{mix}}}{\mathrm{d}t}\right)^{-1}, \tag{12}$$

$$\tau_{\mathrm{dil,det}} = \frac{h_{\mathrm{mix}}}{w_e}, \tag{13}$$

$$\tau_{\mathrm{dil,dif}} = \left(\frac{1}{\sigma_y\sigma_z}\frac{\mathrm{d}(\sigma_y\sigma_z)}{\mathrm{d}t}\right)^{-1}. \tag{14}$$

Here w_{e} is the entrainment velocity, whereas σ_y and σ_z are the horizontal and vertical plume dispersion parameters which depend on atmospheric stability and the plume travel time (Kerminen and Wexler, 1995a).

The timescale over which the mean diameter of the nucleation mode changes, $(1/d_{\mathrm{nuc}} \times \mathrm{d}d_{\mathrm{nuc}}/\mathrm{d}t)^{-1}$, can be split into that due to the production of new nuclei, that due to the growth of nuclei by condensation and that due to their growth by self-coagulation. The first of these timescales is obtained directly from eq. (2):

$$\tau_{\mathrm{d,prod}} = \frac{N_{\mathrm{nuc}}d_{\mathrm{nuc}}}{J_{\mathrm{nuc}}(d_{\mathrm{nuc}} - d^*)} = \frac{d_{\mathrm{nuc}}}{(d_{\mathrm{nuc}} - d^*)}\tau_{\mathrm{prod}}. \tag{15}$$

This scale approaches infinity when the production rate of nuclei is very low, or when the new nuclei are approximately the same size as the pre-existing nuclei. The two growth timescales are obtained by substituting eqs. (3) and (5) into the first term in the right-hand side of eq. (2), respectively:

$$\tau_{\mathrm{G,cond}} = \frac{\rho_{\mathrm{nuc}}d_{\mathrm{nuc}}^2}{4\sum_i D_i\beta(Kn, \alpha_i)[C_i - C_{i,eq}(d_{\mathrm{nuc}})]}, \tag{16}$$

$$\tau_{\mathrm{G,scoa}} = \frac{3}{K(d_{\mathrm{nuc}}, d_{\mathrm{nuc}})N_{\mathrm{nuc}}}. \tag{17}$$

By comparing eqs. (9) and (17), one may notice that $\tau_{\mathrm{G,scoa}}$ and $\tau_{\mathrm{R,scoa}}$ are related to each other via $\tau_{\mathrm{G,scoa}} = 1.5 \times \tau_{\mathrm{R,scoa}}$. The overall timescale for the growth of nuclei, after taking into account both self-coagulation and condensation, is simply $\tau_{\mathrm{G}}^{-1} = \tau_{\mathrm{G,cond}}^{-1} + \tau_{\mathrm{G,scoa}}^{-1}$.

In order to couple the nuclei growth and their removal, we need a timescale which is that over which the scavenging rate changes due to the nucleus growth, τ_{rrate}. In cases where the nuclei are removed mainly by coagulation with larger particles, we may write

$$\tau_{\mathrm{rrate}} = \left(\frac{1}{\mathrm{CoagS}(d_{\mathrm{nuc}})}\frac{\mathrm{d\,CoagS}(d_{\mathrm{nuc}})}{\mathrm{d}t}\right)^{-1} \approx \frac{1}{k}\left(\frac{1}{d_{\mathrm{nuc}}}\frac{\mathrm{d}d_{\mathrm{nuc}}}{\mathrm{d}t}\right)^{-1} = \frac{\tau_G}{k}. \tag{18}$$

In deriving this, we have made use of the fact that $K(d_{\mathrm{nuc}}, d_j)$ is proportional to d_{nuc}^{-k}, with k varying in the range 1.5–2 depending slightly on d_{nuc} and the particle size distribution (Kerminen and Kulmala, 2002). Since τ_{rrate} and τ_{G} are of the same magnitude, we may conclude that it is sufficient to compare the timescales τ_{G} and $\tau_{\mathrm{R,coag}}$ when estimating the relative importance of the growth of nuclei and their removal into larger particles. Using the same arguments it can be shown that the relative importance of the growth of nuclei and their surface deposition can be estimated by comparing the timescales τ_{G} and $\tau_{\mathrm{R,dep}}$.

The time evolution of low-volatile vapour concentration, given by eq. (6), is dependent on three timescales. The most important of these is a so-called condensation timescale that is the inverse of the condensation sink (Kerminen and Wexler, 1995a; Kulmala et al., 2001b):

$$\tau_{\infty} = \frac{1}{\mathrm{CS}}. \tag{19}$$

The two other timescales are those over which the vapour production rate and the condensation sink change (Kerminen and Wexler, 1995a):

$$\tau_{\mathrm{p}} = \left(\frac{1}{P_i}\frac{\mathrm{d}P_i}{\mathrm{d}t}\right)^{-1}, \tag{20}$$

$$\tau_{\mathrm{a}} = \left(\frac{1}{\mathrm{CS}}\frac{\mathrm{dCS}}{\mathrm{d}t}\right)^{-1}. \tag{21}$$

The magnitude of τ_{p} is dependent on how fast the concentrations of gaseous precursors (SO_2 and semi-volatile organic vapours), their atmospheric oxidation rate and their low-volatile vapour yield change over the course of the day. The timescale τ_{a} is related to changes in the pre-existing particle size distribution, being dependent on dilution (governed by the timescale τ_{dil}) and other processes able to influence the concentration and/or the size of pre-existing particles.

3. Application to the atmosphere

A number of timescales associated with the dynamics of a nucleation mode have been introduced. In this section we demonstrate how to apply these timescales to real atmospheric systems and, with the help of them, discuss briefly which processes are important under different environmental conditions. Before doing the analysis, we make a few simplifying assumptions and discuss their limitations. We also verify our timescale approach by comparing its predictions to those obtained from a numerical model that accurately simulates the nucleation mode dynamics.

3.1. *Assumptions*

By acting as a sink for both nuclei and condensable vapours, pre-existing larger particles (particles with diameters >20 nm) play a central role in determining the dynamics of a nucleation mode. Here we describe these larger particles using a single measure, the condensation sink CS. Using the "model" size distributions adopted from Jaenicke (1993) (see Table 1) together with eq. (7), we obtain values of CS equal to 6.4×10^{-4}, 2.8×10^{-3}, 6.9×10^{-3} and 2.0×10^{-2} s^{-1} for marine, rural, remote continental and urban aerosols, respectively. Repeating similar calculations using the available literature data (O'Dowd et al., 1997; Morawska et al., 1999; Heintzenberg et al., 2000; Mäkelä et al., 2000; Raes et al., 2000; Väkevä et al., 2000), we may conclude that typical condensation sinks are <0.001 s^{-1} for marine aerosol systems, between about 0.001 and 0.01 s^{-1} for remote continental and rural aerosol systems and >0.01 s^{-1} for urban aerosol systems. In our later analysis, these three CS regimes are used to cover all lower-tropospheric aerosol systems (see Table 1). The shape of the larger particle size distribution is assumed to follow that of Jaenicke (1993) in each of these regimes, but the total particle number concentration is varied to obtain different values of CS.

Two simplifying assumptions will be made concerning the condensable vapours responsible for the growth of nuclei. First, we assume that these vapours condense irreversibly not only into larger pre-existing particles but also to the nucleation mode. This makes it easier to calculate the nuclei growth timescale due to condensation, since we may assume that C_i is large compared with $C_{i,eq}$ in eq. (16). The drawback is that we cannot deal with all potentially important processes associated with the dynamics of the smallest nuclei. The second assumption is that the timescales τ_{p} and τ_{a} given by eqs. (20) and (21) are much longer than the condensation timescale τ_{∞} given by eq. (19). When this is the case, the vapour concentrations C_i rapidly approach a pseudo-steady state (e.g. Kerminen and Wexler, 1995b):

Table 1. Size distribution parameters used to describe the larger particle population in marine, rural and urban environments. The modal parameters (geometric mean diameter d_{mean}, geometric standard deviation σ_{g} and particle number concentration N) have been taken from Jaenicke (1993) with two exceptions: (1) no nucleation mode has been included and (2) the modal particle number concentration has been allowed to vary to cover the range of condensation sinks typical for each environment

Environment	Marine	Rural	Urban
Condensation sink, s^{-1}	<0.001	0.001–0.01	>0.01
$d_{\mathrm{mean,1}}$ (μm)	0.266	0.054	0.05
$d_{\mathrm{mean,2}}$ (μm)	0.58	0.084	
$\log \sigma_{\mathrm{g,1}}$	0.21	0.56	0.34
$\log \sigma_{\mathrm{g,2}}$	0.40	0.27	
N_1 (particles cm^{-3})	<100	51–510	$>1.8 \times 10^4$
N_2 (particles cm^{-3})	<5	710–7100	

$$C_{i,\mathrm{ss}} \approx P_i \tau_{\infty} = \frac{P_i}{\mathrm{CS}}. \tag{22}$$

Equation (22) provides a good approximation to low-volatile vapour concentrations in most lower-tropospheric environments (Kerminen and Wexler, 1995a,b), even though it may fail if τ_{∞} is very large (clean air) or if τ_{p} or τ_{a} are very small (as might be the case in young power plant plumes or just after the sunrise when P_i may change very rapidly). Anyway, eq. (22) makes it possible to estimate vapour concentrations from the corresponding gaseous production rates, which is quite useful, for example, in many modelling approaches.

3.2. *Removal of nuclei*

Nucleation mode particles can be removed by self-coagulation (characterized by the timescale $\tau_{\mathrm{R,scoa}}$), by coagulation with larger pre-existing particles ($\tau_{\mathrm{R,coag}}$) and by surface deposition ($\tau_{\mathrm{R,dep}}$). The two coagulation mechanisms are compared with each other in Fig. 1, which demonstrates that factors favouring self-coagulation are a high nuclei number concentration (large N_{nuc}), large mean size of the nucleation mode (large d_{nuc}) and low number concentration of pre-existing background particles (small CS). In most cases, unusually high nucleation mode particle number concentrations are needed to make their removal by self-coagulation as efficient as their removal by coagulation with larger particles. Potential environments which are significant affected by self-coagulation are certain coastal areas characterized by very strong nucleation bursts (O'Dowd, 2001), as well as urban areas characterized by a relatively low amount of background pollution together with high emissions of large ($d_{\mathrm{nuc}} \sim 20$ nm) nucleation mode particles by local traffic.

A comparison between the timescales $\tau_{\mathrm{R,coag}}$ and $\tau_{\mathrm{R,dep}}$ demonstrates that scavenging of nuclei by surface deposition is

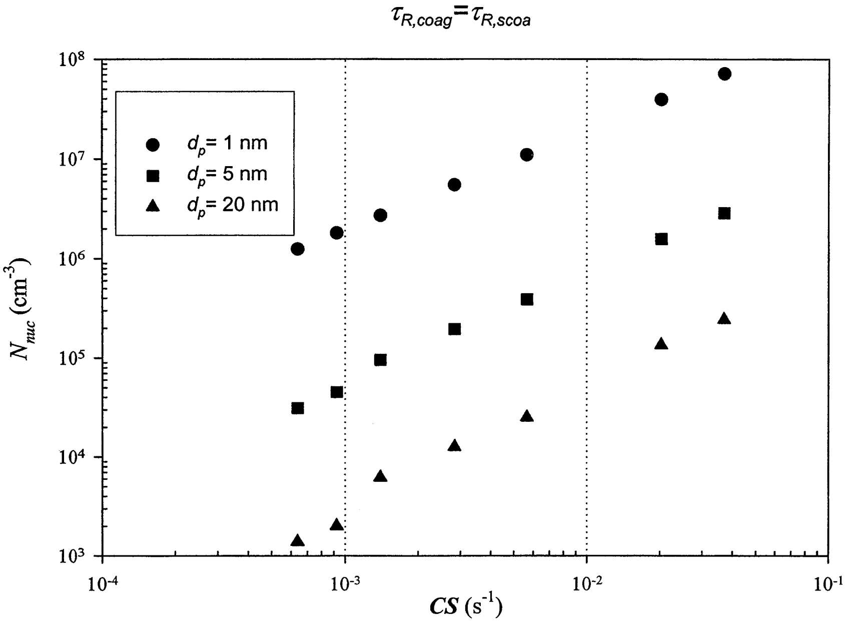

Fig. 1. The nuclei number concentration that is required to make the timescale $\tau_{\mathrm{R,scoa}}$ equal to the timescale $\tau_{\mathrm{R,coag}}$. The condensation sink is allowed to vary between 0.0001 and 0.1 s^{-1} and the mean diameter of the nucleation mode has been assumed to be equal to 1, 5 or 20 nm. In the region above each line, removal by self-coagulation dominates over that by coagulation with larger particles.

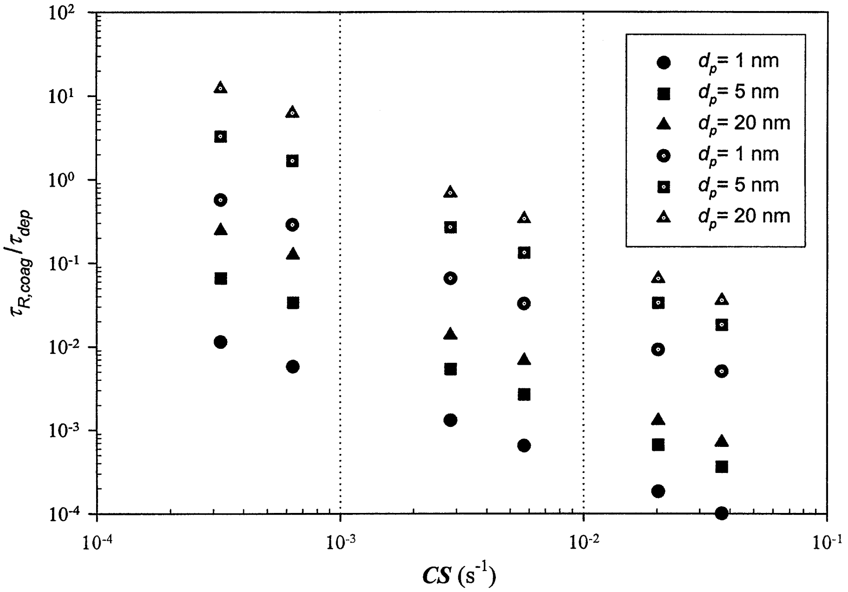

Fig. 2. The ratio of the timescales $\tau_{\mathrm{R,coag}}$ and $\tau_{\mathrm{R,dep}}$ as a function of condensation sink and for different mean nucleation mode diameters. Cases representing "slow" (solid symbols; $h_{\mathrm{mix}} = 1000$ m, wind speed = 2 m s^{-1}) and "fast" (open symbols; $h_{\mathrm{mix}} =$ 100 m, wind speed = 10 m s^{-1}) deposition have been illustrated. The particle deposition velocity has been calculated using the parametrization of Slinn and Slinn (1980).

almost always much slower than that by coagulation with larger particles (Fig. 2). Clearly, the surface deposition of nuclei must be taken into account under very extreme conditions only which are a low mixed layer height combined with relatively clean air and large mean size of the nucleation mode.

3.3. *Growth of nuclei*

In the previous section we showed that under most atmospheric conditions, the dominant removal mechanism for atmospheric nucleation mode particles is their coagulation with larger particles. Removal of the nuclei is tied strongly to their growth to larger sizes by condensation and self-coagulation. If the nuclei grow very slowly ($\tau_{\mathrm{G}} \gg \tau_{\mathrm{R,coag}}$), they are scavenged away and have practically no atmospheric relevance. If, however, the nuclei grow fast enough ($\tau_{\mathrm{G}} \lesssim \tau_{\mathrm{R,coag}}$), a significant fraction of them can survive and eventually modify the whole particle population.

We consider two relevant growth timescales, $\tau_{\mathrm{G,cond}}$ and $\tau_{\mathrm{G,scoa}}$, which are compared with $\tau_{\mathrm{R,coag}}$ in Figs. 3 and 4, respectively. Starting from growth by condensation, let us first concentrate on sulfuric acid, which is the most studied compound with respect to formation and growth of new particles. Gaseous sulfuric acid is formed by the reaction of sulfur dioxide (SO_2) with the hydroxyl radical (OH). Ambient SO_2 concentrations are usually

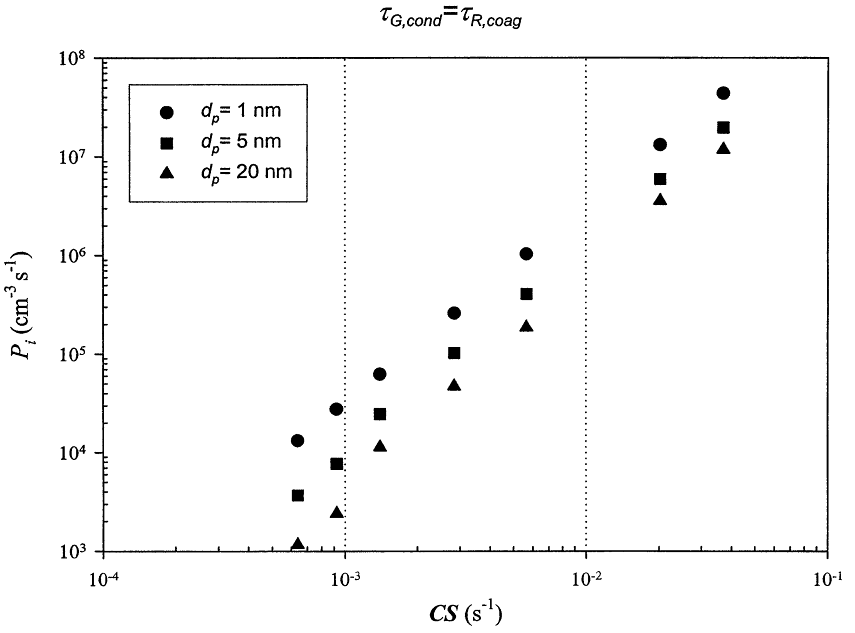

Fig. 3. The condensable vapour production rate that is required to make the timescales $\tau_{\mathrm{G,cond}}$ and $\tau_{\mathrm{R,coag}}$ equal to each other. The timescale $\tau_{\mathrm{G,cond}}$ has been calculated by assuming C_i to be dependent on P_i via the relation (22). The mass accommodation coefficient, gas-phase diffusion coefficient and molecular weight of the condensing vapour have been set equal to 1, 0.1 cm^2 s^{-1} and 100 g mol^{-1}, respectively.

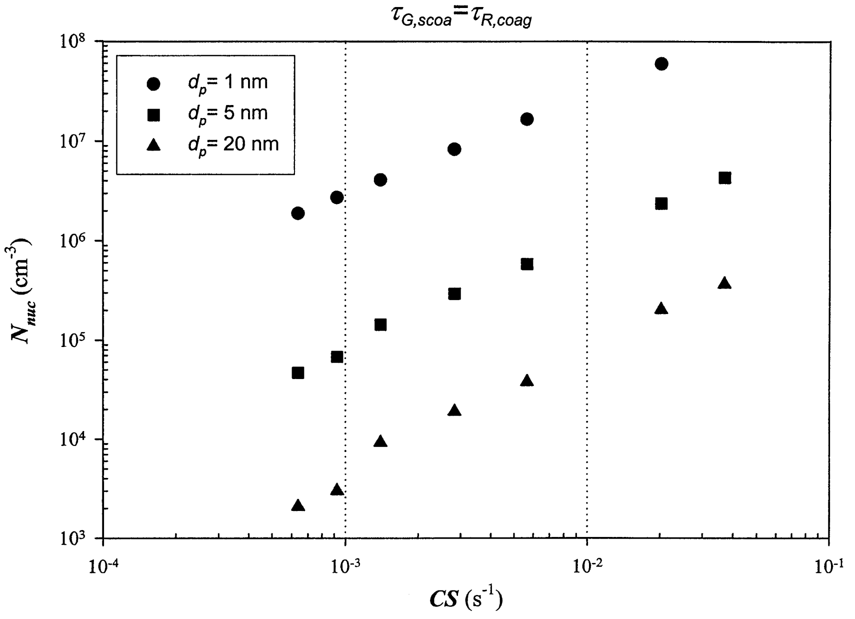

Fig. 4. The nuclei number concentration that is required to make the timescales $\tau_{\mathrm{G,scoa}}$ and $\tau_{\mathrm{R,coag}}$ equal to each other.

below 0.1 ppb in marine areas, between about 0.1 and 5 ppb in rural areas and between about 1 and 50 ppb in urban areas (Sickles, 1999; Thornton et al., 1999; Redington and Derwent, 2002). By noting that daytime OH radical concentrations vary in the range (1–5)× 10^6 molecules cm^{-3} over mid latitudes (Spivakovski et al., 2000), we estimate that typical daytime production rates for gaseous sulfuric acid are well below 10^4 molecules cm^{-3} s^{-1} in marine areas, between about 2 × 10^3 and 6 × 10^5 molecules cm^{-3} s^{-1} in rural areas and between about 2 × 10^4 and × 10^6 molecules cm^{-3} s^{-1} for urban areas. The timescales for growth of nuclei resulting from these production rates are longer than the respective scavenging timescales, especially for very small nuclei (see Fig. 3). Noting further that compounds co-condensing with sulfuric acid (water vapour and ammonia) influence $\tau_{\mathrm{G,cond}}$ only marginally, we may conclude that the growth of nuclei due to gaseous sulfuric acid can rarely compete with the scavenging of nuclei by coagulation. Exceptions to this are certain rural and urban areas, in which relatively high SO_2 concentrations may co-exist with sufficiently low pre-existing particle number concentrations (Birmili and Wiedensohler, 2000; Birmili et al., 2000; Coe et al., 2000; Harrison et al., 2000; Woo et al., 2001).

In addition to sulfuric acid, very few other inorganic gases have been identified which might significantly contribute to the growth of nuclei. One potentially important compound class might be condensable iodine vapours formed in the marine boundary layer, but the exact chemistry and rate of production of these compounds remain to be quantified (O'Dowd et al., 2002). In forested areas, strong yet indirect evidence has been obtained suggesting that the bulk growth of nuclei is caused by organic vapours resulting from the oxidation of monoterpenes (Marti et al., 1997; Kavouras et al., 1998; Leaitch et al., 1999; Yu et al., 1999; Kulmala et al., 2001a). Unfortunately, neither the identity nor the atmospheric chemistry of these vapours has been established. Kulmala et al. (2001b) analysed a few nucleation events in a boreal forest in Finland and estimated that the overall source rate of low-volatile organic vapours needed to explain the observed particle growth was of the order 10^5 molecules $\mathrm{cm}^{-3}\ \mathrm{s}^{-1}$. Since typical condensation sinks during these events were of the order of 0.003 s^{-1}, we obtain timescales for the growth of nuclei that are comparable to the respective scavenging timescales (see Fig. 3). It appears that the removal of nuclei by coagulation with larger particles needs to be taken into account in practically all cases where nucleation is followed by growth into larger sizes.

When comparing the growth of nuclei by self-coagulation and their removal by coagulation with larger background particles (Fig. 4), the size of the nucleus plays a very important role. We can see that the growth of nanometre-sized nuclei by self-coagulation cannot compete with their removal unless the nuclei number concentration is exceptionally high ($>10^6$ molecules cm^{-3}). On the other hand, if the nuclei are able to grow initially by condensation without decreasing very much in number, self-coagulation may also eventually become an important growth process.

The above analysis demonstrates that the removal of very small nuclei by coagulation into larger particles dominates over the growth of nuclei by self-coagulation and condensation due to gaseous sulfuric acid, at least under condition typical for the lower troposphere. This has two important consequences. First, removal by coagulation is likely to be the single most important process limiting the formation of new particles in the atmospheric boundary layer. Second, condensing vapours other than sulfuric acid are likely to play a central role in the early growth of small nuclei formed in the atmosphere. Both these findings are consistent with suggestions made by other researchers based on atmospheric measurement data.

3.4. *Production and dilution of nuclei*

When the nucleation mode is already present, production of new nuclei can be neglected if it is too slow to produce a significant number of new nuclei. This condition can be expressed mathematically as $\tau_{\mathrm{prod}} \gg \Delta t$, where Δt is the relevant timescale of the problem such as the duration of the simulated event. Production of nuclei can also be neglected if the change in the total nuclei number concentration is governed by scavenging or dilution. This condition can be written as $\tau_{\mathrm{prod}} \gg \mathrm{MIN}(\tau_{\mathrm{R,scoa}}, \tau_{\mathrm{R,coag}}, \tau_{\mathrm{R,dep}}, \tau_{\mathrm{dil}})$.

If the production of nuclei is fast enough, the timescale $\tau_{\mathrm{d,prod}}$ may become comparable with or smaller than the nuclei growth timescale τ_{G}. When this is the case, the number mean diameter of the nucleation mode may remain unchanged or even decrease despite the continuous growth of pre-existing nuclei. This kind of a situation is very difficult from the modelling point of view, especially when using modal techniques, and thus is worth recognizing.

In some situations, dilution of the concentration of nuclei by boundary layer growth, detrainment or turbulent diffusion may dominate over the scavenging and growth of nuclei. These situations can be identified by comparing the timescales given by eqs. (12)–(14) to the respective scavenging and growth timescales. Dilution of nucleation mode particles might become important in continental boundary layers after sunrise (Nilsson et al., 2001), in power plant plumes entraining into unstable boundary layers (Kerminen and Wexler, 1995a) or in young plumes coming from busy traffic routes (Shi et al., 1999; Zhu et al., 2002).

3.5. *Verification of the timescale approach using a detailed numerical model*

In order to verify the applicability of the timescale approach and to provide some quantitative criteria concerning the relative importance of different processes affecting the nucleation mode, a detailed aerosol dynamical model developed by Lehtinen and Kulmala (2003) was applied. In the original model, the size spectrum is completely discretized molecule-by-molecule, with the aim of avoiding numerical diffusion problems completely. Here we employed a discrete-sectional version of the code, in which the diameter interval ranging from one molecule to 27 nm is divided into 200 discrete (molecule-by molecule) bins and 800 sectionally spaced bins. This modification was necessary in order to perform the simulations within a reasonable time frame.

As a first example, we looked at the growth of a nucleation mode by simultaneous self-coagulation and condensation. The relevant timescales in these kinds of simulations are $\tau_{\mathrm{G,cond}}$ and $\tau_{\mathrm{G,scoa}}$. When the ratio $\tau_{\mathrm{G,cond}}/\tau_{\mathrm{G,scoa}}$, denoted by r, was below 0.1 (Figs. 5a and 5b), the growth was dominated almost entirely by condensation. This can be seen by comparing the end size distribution resulting from full aerosol dynamics with that resulting from condensation only. A slight effect due to self-coagulation in the $r = 0.1$ case is visible as the formation of a tail in the larger end of the size distribution. The effect of self-coagulation became clearer when r increased to unity (Fig. 5c). In this case the peak location of the distribution was still predicted quite reasonably using a pure condensation model, but its shape was completely wrong without including self-coagulation. When r reached a value of 10 (Fig. 5d), neither of the two process models worked well by themselves. Finally, when r approached a value of 100 (Fig. 5e), the dynamics was dominated by self-coagulation. Summarizing, condensation seems to dominate the growth of a nucleation mode for $\tau_{\mathrm{G,cond}}/\tau_{\mathrm{G,scoa}} < 0.1$–$0.2$,

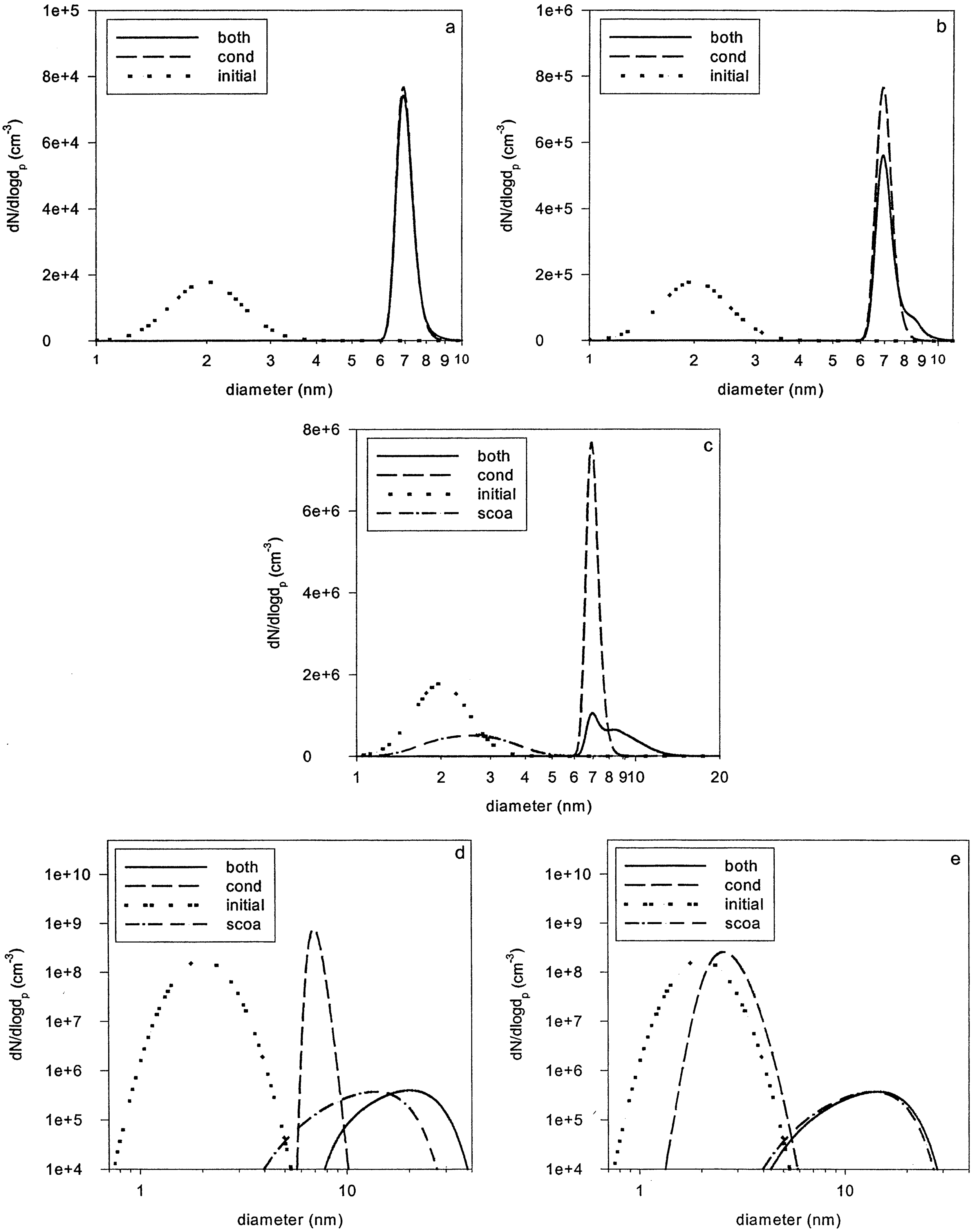

Fig. 5. Growth of nucleation mode particles by simultaneous condensation and self-coagulation (both), and when only either of these two processes (cond or scoa) has been included. The simulations were started with a log-normal particle size distribution peaking at 2 nm. The overall simulation time was 1 h, after which the final size distributions were plotted. The conditions were chosen such that the ratio $\tau_{\mathrm{G,cond}}/\tau_{\mathrm{G,scoa}}$ was equal to 0.01 (a), 0.1 (b), 1 (c), 10 (d) and 100 (e) at the beginning of each simulation.

allowing self-coagulation to be neglected in these cases. Self-coagulation alone does not describe the behaviour of the system very well until $\tau_{\mathrm{G,cond}}/\tau_{\mathrm{G,scoa}}$ reaches values >50–100.

The second example concerns competition between condensational growth and removal by coagulation, aiming to find out if a characteristic timescale analysis can point out the situations in which nucleation mode particles can grow into the Aitken mode range before being scavenged by pre-existing background particles. The relevant timescales were now $\tau_{\mathrm{G,cond}}$ and $\tau_{\mathrm{R,coag}}$, and their ratio $\tau_{\mathrm{G,cond}}/\tau_{\mathrm{R,coag}}$ was denoted by s. We may see that removal by coagulation remained insignificant for s up to about 0.1–0.2, but became increasingly important thereafter (Fig. 6). The decrease in the nuclei number concentration during their growth was almost three orders of magnitude for s equal to 5, and more than five orders of magnitude for s equal to 10. We may conclude that for $\tau_{\mathrm{G,cond}}/\tau_{\mathrm{R,coag}}$ greater than about 10,

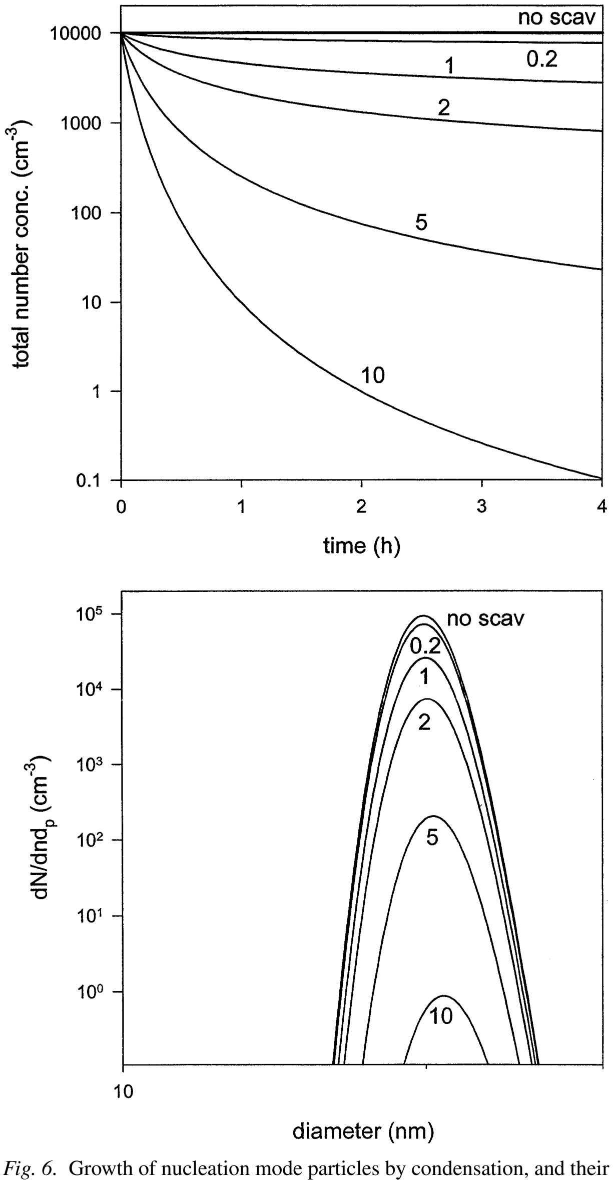

Fig. 6. Growth of nucleation mode particles by condensation, and their removal by coagulation with background particles. The simulations were started with a log-normal size distribution peaking at 3 nm and continued until the mean diameter of the mode reached 20 nm. Both the time evolution of the nuclei number concentration (top) and the final nuclei size distribution (bottom) are shown. The conditions were chosen such that the ratio $\tau_{\mathrm{G,cond}}/\tau_{\mathrm{R,coag}}$ varied in the range 0.2–10, as shown beside each curve in the figure.

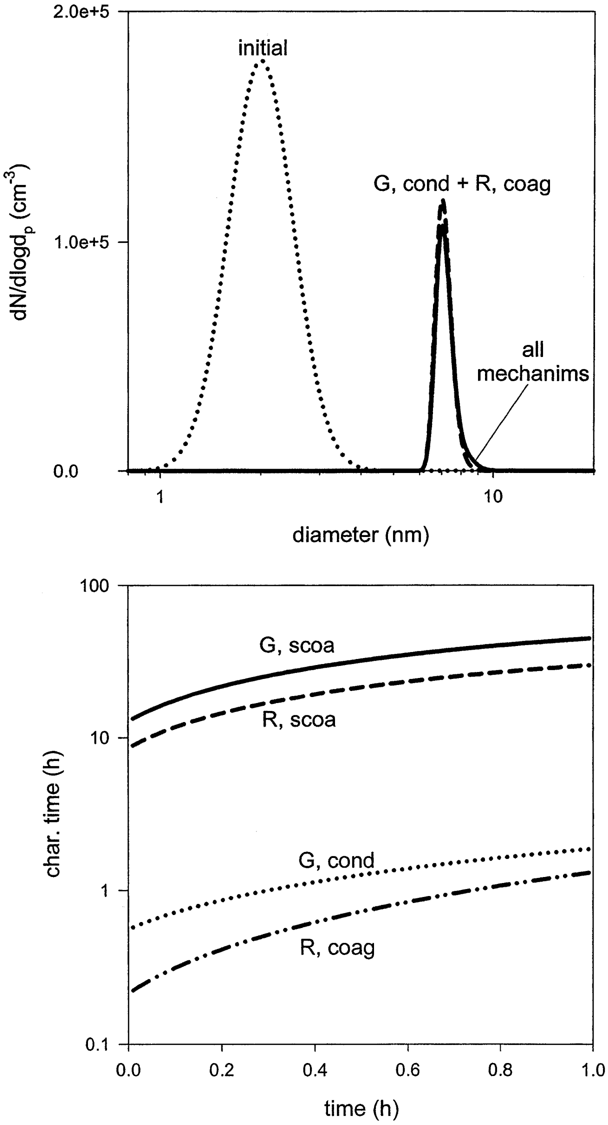

Fig. 7. Growth of nucleation mode particles by simultaneous condensation and self-coagulation, and their removal by coagulation with background particles. The simulations were started with a log-normal size distribution peaking at 3 nm and continued until the mean diameter of the mode reached 20 nm. The figure shows the initial and final nuclei number size distributions (top), as well as the time evolution of the relevant timescales.

condensational growth of nucleation mode particles need not usually be considered, as very few or none of the particles ever reach meaningful sizes.

The third case exemplifies a full simulation in which several of the characteristic timescales were utilized in finding out the important dynamical mechanisms. The purpose was to reveal, through a timescale analysis, what is the main growth and scavenging mechanism and if a significant number of particles reach meaningful sizes, in this case assumed to be the lower boundary of the Aitken mode at 20 nm. The detailed model results were then compared with a simplified model, in which unimportant processes (based on the timescale analysis) were left out of consideration. The results are shown in Fig. 7. Based on timescales, self-coagulation is expected to be unimportant for both growth ($\tau_{\mathrm{G,scoa}}$ was also about 10 times larger than $\tau_{\mathrm{G,cond}}$) and removal ($\tau_{\mathrm{R,scoa}}$ was about 10 times larger than $\tau_{\mathrm{R,coag}}$) of the nucleation mode particles. Results from numerical simulations confirmed this feature: the final size distribution obtained using the simplified model, i.e. in which self-coagulation is completely neglected (both in the sense of growth as well as removal), was a very good approximation to that obtained using a detailed model with all processes included. The rather similar magnitude of $\tau_{\mathrm{G,cond}}$ and $\tau_{\mathrm{R,coag}}$ suggests further that both condensational growth and coagulational removal of nucleation mode particles are important for the system. This can easily be seen to be the case when comparing the initial and final size distributions from a detailed model with each other.

4. Summary and conclusions

A theoretical framework was constructed by which one can estimate the relative role of different processes in the dynamics of atmospheric nucleation mode particles. The framework relies on 14 timescales that describe (1) changes in the total nuclei number concentration, (2) changes in the mean diameter of the nucleation mode and (3) concentrations of low-volatile vapours responsible for the growth of nuclei. The magnitude of the derived timescales can be calculated relatively easily from the available measurement or modelling data.

Application to different environments in the lower troposphere revealed that under most conditions, removal of nuclei is dominated by coagulation with larger background particles. Removal of nuclei by self-coagulation may be important in coastal areas characterized by very strong nucleation bursts, as well as urban areas characterized by a relatively low amount of background pollution together with high emissions of large nucleation mode particles by local traffic. Surface deposition of nuclei must be taken into account under very extreme conditions only, which are a low mixed layer height combined with relatively clean air and a large mean size of the nucleation mode.

According to the timescale analysis, there is usually very strong competition between the growth of nuclei by condensation and their removal by coagulation. It thus appears that the removal of nuclei needs to be taken into account in practically all cases in which nucleation is followed by growth into large sizes. In many cases, the nucleation mode is likely to fade away altogether before reaching sizes important for atmospheric chemistry or physics. The growth of nuclei by self-coagulation alone can rarely compete with their removal by coagulation with background particles.

By comparing predictions based on relevant timescales with those obtained from detailed numerical simulations, general criteria were derived concerning (1) when one may neglect nuclei self-coagulation when looking at nucleation mode dynamics and (2) when the whole nucleation mode can be neglected because of its eventual removal. These criteria are extremely useful for atmospheric modellers who need to simplify their models as much as possible. From the modelling point of view, other processes requiring care are the introduction of new nuclei into the system and a decrease in nuclei number concentration due to dilution of the air. The situations in which these processes may become comparable to, or even dominate over, the removal or growth of nuclei can also be identified using timescale analysis.

It should finally be kept in mind that there may be other, as yet poorly quantified processes, that affect the dynamics of a nucleation mode but are not a part of the theoretical framework developed here. Examples of such processes include various heterogeneous reactions taking place on the surfaces of nuclei (Jang et al., 2002; Zhang and Wexler, 2002b), the influence of ions on the growth of nuclei (e.g. Yu and Turco, 2001) and the activation of nuclei by new condensable vapours during their growth (Kulmala et al., 2004a). Since most of these processes are expected to be most effective for very small nuclei, extreme care should be taken before applying the timescale analysis to nucleation modes located below a particle diameter of some 3–4 nm.

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