



Gas-to-particle conversion in the atmosphere: I. Evidence from empirical atmospheric aerosols

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Abstract

Condensable vapours such as sulphuric acid form aerosol in the atmosphere by the competing mechanisms of condensation on existing aerosol and the nucleation of new aerosol. Observational and theoretical evidence for the relative magnitudes of the competing processes is reviewed, and a number of general conclusions are made. Condensation is sensitive to the sticking probability of sulphuric acid molecules on aerosol particles, but there is now good evidence that it should be close to unity. In this case, equilibration timescales between acid vapour and the aerosol in most of the atmosphere are of the order of minutes or less, so that the acid concentration on such timescales given simply by the production rate times the equilibration time. When the acid concentration exceeds a threshold, nucleation will occur. The atmospheric aerosol therefore follows a history of initial formation in a nucleation burst followed by growth and coagulation with final removal by precipitation. This leads to the inverse correlation between aerosol number concentration and mass concentration found by Clarke (1992. *Journal of Atmospheric Chemistry* 14, 479–488) in the free troposphere. Binary homogeneous nucleation of sulphuric acid/water droplets, for which various simplified rates are compared, may dominate in such regions, but other mechanisms are possible elsewhere. A detailed analysis is performed of the number concentrations, removal rates, and masses of the components of the different types of global aerosols proposed empirically by Jaenicke (1993. *Tropospheric Aerosols, Aerosol-Cloud-Climate Interaction*. Academic Press, New York). There is a striking correlation between number concentrations in the nucleation and accumulation modes; and the giant aerosol mode, which if it is present dominates the mass, has little effect on the gas-to-particle conversion process. The mass of the atmospheric aerosol is therefore uncorrelated with the magnitude of molecular aerosol removal by condensation. © 1998 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Gases emitted into the atmosphere may be converted into condensable molecular species, for example the formation of sulphuric acid from SO₂. Aerosol number

concentrations and mass densities may then be increased by the sulphate produced. This is the basis of the model of Langner and Rodhe (1991) for the atmospheric sulphur cycle. The aerosol scatters solar radiation directly and the number of cloud condensation nuclei (CCN) will be increased. Using assumptions for the number and size of sulphate particles produced, Jones et al. (1994) have shown that considerable radiative forcing in a cooling

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direction may arise from the increase in CCN. The aim of this and a companion paper (Clement and Ford, 1998) referred to as paper II, is to describe current information on aerosol nucleation and formation mechanisms in the atmosphere, in order to estimate the extra particle production due to increased input of condensable material into the atmosphere.

In this first paper we summarise available information on nucleation and growth, and follow previous work by Kerminen and Wexler (1995b) to relate growth laws and empirical data to models for molecular concentrations. The aspects focussed on here are the sensitivity of equilibrium timescales to molecular sticking probabilities, the consistency of simple parametrisations of the binary nucleation rate for sulphuric acid/water, and information on nucleation and growth which can be obtained from the empirical characterisation of global atmospheric aerosols by Jaenicke (1993). Since nucleation probably occurs in bursts with short timescales, it is highly desirable for global modelling to describe these with analytical models. In the paper II we describe such models in which nucleation rates are parametrised with a power law dependence on acid vapour concentration (Easter and Peters, 1994).

Although the principal condensable material that we discuss here is sulphuric acid, it is worth stating that the amount of ammonia present and concentration of ammonium sulphate produced directly may be important for aerosol production (Weber et al., 1996). Also, the input of NO_x into the atmosphere is increasing faster than the input of SO_2 , and there have been suggestions that the nitric acid vapour produced will have similar effects to sulphuric acid (Kulmala et al., 1993a, 1995).

In Section 2, we begin to describe the tropospheric aerosol and its properties by referring to recent review articles by Jaenicke (1993). A similar, but not so quantitative description of the tropospheric aerosol has been given by Pandis et al. (1995). The main processes involving gas-to-particle conversion are condensation upon an existing aerosol and nucleation of new aerosol, processes which are in competition. It is therefore essential to examine how well these processes are presently understood, and Sections 3 and 4 are devoted to aerosol growth and nucleation, respectively. In particular, we look at the sensitivity of aerosol growth rates to the sticking probability of sulphuric acid molecules. Estimated values for this parameter have varied greatly, but arguments have recently been given that it should be close to unity (Clement et al., 1996).

In Section 4 we describe and compare various simplified expressions which have been used for the binary homogeneous nucleation of sulphuric acid/water droplets. For atmospheric modelling such simplified expressions are highly desirable. The sensitivity of the results to the nucleation expressions can then be examined directly.

Because of the sensitivity of nucleation rates to the acid concentration, fluctuations in the atmosphere play a major role in determining where and when nucleation takes place. This subject is examined briefly, especially regarding fluctuations in aerosol concentrations which are often due to precipitation. The history of an air parcel involving precipitation and nucleation fluctuations and the competition between aerosol growth and nucleation is reiterated: a preliminary account was previously presented (Clement and Ford, 1996). This explains the observation of an inverse correlation between aerosol number concentration and mass concentration found in the free troposphere (Clarke, 1992). Nucleation mechanisms other than the binary homogeneous nucleation of sulphuric acid/water, for which experimental evidence is presently accumulating, are also considered.

The basic equation for concentrations of sulphuric acid molecules is described in Section 5, and the removal rate for condensation on existing aerosol is evaluated for the set of different types of global aerosols quantified by Jaenicke (1993). This gives a clear picture of removal rate timescales onto the aerosols with different proposed values for the molecular sticking probability. Molecular concentrations can then be predicted by this equation in the absence of nucleation (Kerminen and Wexler, 1995b). Approximate solutions of this equation form the subject of our companion paper II.

A detailed analysis of the global aerosol characterisation of Jaenicke (1993) is performed in Section 6. The analysis leads to some fascinating conclusions regarding the aerosol and its formation and growth from gas-to-particle conversion. Even if some of the characterisation and results turn out not to be accurate, we point out the great utility of the analysis of observational data in terms of moments of the size distribution as a way to learn about the most important aerosol processes in the atmosphere and how to model them.

2. Characteristics of observed aerosols

Any attempt to represent aerosols globally must reproduce the main features of aerosols observed in different parts of the atmosphere. This requirement presents a problem as observed aerosols have very different characteristics in different areas. One simplification (Wilson and Raes, 1996), is to use a minimal number of lognormal modes to represent the aerosol. With lognormal distributions there are three parameters per distribution, number n , size parameter R , and variance σ . Jaenicke (1993) parametrised observed global aerosols using three distributions for each type of aerosol. The size distribution $n(R)$, where R is the particle radius, is given by

$$n(R) = \sum_{i=1}^3 \frac{n_i}{(2\pi)^{1/2} \ln(\sigma_i)} \exp \left\{ -\frac{1}{2} \left[\frac{\ln(R/R_i)}{\ln \sigma_i} \right]^2 \right\} \frac{1}{R}. \quad (1)$$

Table 1
Parameters for models of aerosol size distributions described by the sum of three lognormal functions

Aerosol	Range	<i>i</i>	n_i (cm^{-3})	R_i (μm)	$\ln \sigma_i^a$
Polar	I	1	2.17×10^1	0.0689	0.564
	II	2	1.86×10^{-1}	0.375	0.691
	III	3	3.04×10^{-4}	4.29	0.670
Background	I	1	1.29×10^2	0.0036	1.485
	II	2	5.97×10^1	0.127	0.583
	II	3	6.35×10^1	0.259	0.979
Maritime	I	1	1.33×10^2	0.0039	1.512
	II	2	6.66×10^1	0.133	0.484
	II	3	3.06×10^0	0.29	0.912
Remote continental	I	1	3.20×10^3	0.01	0.371
	I	2	2.90×10^3	0.058	0.500
	II	3	3.00×10^{-1}	0.9	0.875
Desert dust storm	I	1	7.26×10^2	0.001	0.569
	I	2	1.14×10^3	0.0188	1.773
	III	3	1.78×10^{-1}	10.8	1.009
Rural	I	1	6.65×10^3	0.00739	0.518
	I	2	1.47×10^2	0.0269	1.283
	I	3	1.99×10^3	0.0419	0.612
Urban	I	1	9.93×10^4	0.00651	0.564
	I	2	1.11×10^3	0.00714	1.533
	I	3	3.64×10^4	0.0248	0.776

^a $\ln \sigma_i$ is used here instead of $\log_{10} \sigma_i$ used by Jaenicke (1993).

The parameters of the three distributions are shown in Table 1, their ranges referring to size:

- (I) Aitken or nucleation particle mode, $0.001 < R_i < 0.1 \mu\text{m}$,
- (II) large or accumulation particle mode, $0.1 < R_i < 1 \mu\text{m}$,
- (III) giant or coarse particle mode, $R_i > 1 \mu\text{m}$.

The properties of the lognormal distributions can be represented using moments,

$$M_n(i) = \int R^n n_i(R) dR = n_i R_i^n Y_i^n, \quad (2)$$

where the function Y_i is related to σ_i by

$$Y_i = \exp [0.5 (\ln \sigma_i)^2]. \quad (3)$$

Thus the aerosol mass concentration or density is given by

$$c_i = (4\pi\rho_p/3) M_3(i), \quad (4)$$

where for calculations we take the particle density to be $\rho_p = 1 \text{ g cm}^{-3}$. The mean radius is

$$R_{av}(i) = M_1(i)/n_i. \quad (5)$$

For gas-to-particle conversion in the atmosphere, the important moments are M_1 and M_2 which control molecular growth on the aerosol, a subject we now examine in detail.

3. Aerosol growth

Sulphuric acid or other condensable molecules in the atmosphere (and an associated latent heat) will be transferred to aerosol particles or droplets at a rate depending on the vapour concentration. The mass and heat transfer processes (see for example Barrett and Clement, 1988) involve macroscopic diffusion or conduction for large drops (continuum limit), and surface molecular processes for small drops (molecular limit). For sulphuric acid, water condensation also occurs to maintain equilibrium condensed phase activities, so that the problem is one of multicomponent condensation including heat transfer. Although there is much recent theory on the subject (Vesala and Kukkonen, 1992; Vesala and Kulmala, 1993; Kulmala et al., 1993b; Vesala et al., 1997), it has not yet been applied to sulphuric acid/water condensation where the assumption has been that sulphuric acid mass transfer is the limiting process (Van Dingenen and Raes, 1991; Pandis et al., 1994; Pandis et al., 1995). As we shall see in detail below, there has been a large discrepancy between growth rates being used by different authors associated with the value of the molecular sticking probability for sulphuric acid molecules. Recent work (Clement et al., 1996), however, has concluded that the value of this parameter should be unity, but we shall examine much smaller values to assess the effect of this parameter on atmospheric aerosol growth rates.

We consider a vapour with pressure p_a , diffusing with diffusivity D onto a spherical droplet of radius R . In the continuum limit for small supersaturations and small concentration in air, the rate of molecular deposition onto the droplet is

$$J_v = 4\pi R \frac{D}{kT} (p_a - p_s) \quad (6)$$

where ρ_d is the droplet density, k is Boltzmann's constant, and p_s is the vapour pressure at the droplet surface which, for mass transfer limited growth, is given by its equilibrium value, $p_{ae}(T)$, at the ambient temperature T , multiplied by an activity coefficient. This result holds when R is much bigger than the molecular mean free path in air:

$$\lambda = 2D (M_a/2 kT)^{1/2} \quad (7)$$

where M_a is the molecular mass of the vapour. λ is equal to $0.09 \mu\text{m}$ for sulphuric acid in air at 20°C , taking $D = 10^{-5} \text{ m}^2 \text{ s}^{-1}$ as used by Pandis et al. (1994). For very small radii, however, we have

$$J_v = \pi R^2 S_p (8/\pi M_a kT)^{1/2} (p_a - p_s), \quad (8)$$

where S_p is the sticking probability or molecular accommodation coefficient. For intermediate values of the Knudsen number,

$$Kn = \lambda/R, \quad (9)$$

Fuchs and Sutugin (1970) introduced a transition regime correction factor F into the continuum equation (6) to describe this region. Pandis et al. (1994) used the following modified form due to Hegg (1990) and Kreidenweis et al. (1991):

$$F = f(Kn)/\{1 + 1.33 Kn f(Kn) [1/S_p - 1]\}, \quad (10)$$

$$f(Kn) = (1 + Kn)/(1 + 1.71 Kn + 1.33 Kn^2). \quad (11)$$

In the limit of large Kn , FJ_v (continuum) given by Eq. (8) reduces to J_v (molecular) given by Eq. (8) with the factor $(8/\pi)^{1/2} = 1.596$ replaced by $(9/4)^{1/2} = 1.5$, a small change compared to the uncertainty in S_p which is the main problem in defining the growth rate.

There appeared recently to be a theoretical and experimental consensus that sticking probabilities for water and sulphuric acid on liquid droplets are small (Itoh, 1990; Van Dingenen and Raes, 1991). Values quoted for sulphuric acid ranged between 0.02 and 0.09, and, in their model of the relationship between DMS flux and CCN concentration in remote marine regions, Pandis et al. (1994) used a base case value of 0.02 with a test value of 0.05. However, experimental and theoretical evidence from a wide field of surface science, including molecular beam experiments and molecular dynamics simulations, suggests that such small values are extremely unlikely at normal atmospheric temperatures (Clement et al., 1996).

Direct experiments on growing droplets of *n*-propanol/water mixtures give results consistent with $S_p = 1$, the theoretically most likely value for all except very light atoms or molecules on dense materials at normal temperatures. Recent measurements of the growth rates of ultra-fine particles at remote marine and continental sites (Weber et al., 1996, 1997) are consistent with $S_p = 1$ for sulphuric acid. Since the evidence for S_p that is much less than unity is generally reliant on complex modelling subject to alternative interpretations, we much prefer values close to unity.

To illustrate the consequent uncertainty in growth rates and molecular removal from the atmosphere, we have calculated the factor F over a range of Kn values and related aerosol radii for three values of S_p . The results are shown in Fig. 1. For $S_p = 1$, growth is controlled by diffusion for R above about $0.2 \mu\text{m}$ at which size growth rates with the smaller values of S_p are considerably lower. At smaller sizes, indicated by the straight line regions, the reduction factors are proportional to S_p . As most of the atmospheric aerosol is in the range $0.01\text{--}1 \mu\text{m}$, growth rates have an uncertainty of over a factor of 10 for nearly all the aerosol if S_p is undetermined.

Furthermore, the change in the slopes of the $S_p = 1$ and $S_p = 0.1$ curves in the accumulation mode region between $R = 0.1 \mu\text{m}$ and $1 \mu\text{m}$ affects the acid condensation on aerosol in this mode relative to that on smaller sized aerosol. In their modelling of sulphate particle growth in the marine boundary layer, Kerminen and Wexler (1995a) found it necessary to use high values of S_p for smaller particles, but their assumption that growth

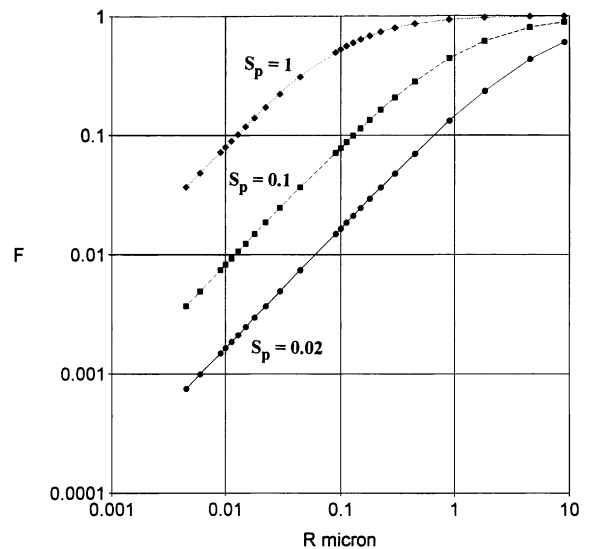


Fig. 1. Factor F which reduces the droplet growth rate from its continuum regime value (at large radius) as a function of droplet radius R for three values of the sulphuric acid molecular sticking probability S_p .

on supermicron sea salt particles is limited by surface area (Kerminen and Wexler, 1997) is suspect when $S_p = 1$. A smaller sea salt particle sink could go some way to alter their finding (Kerminen and Wexler, 1997) that small nuclei cannot grow into CCN over their lifetime.

4. Nucleation

4.1. Simple formulae

The formation of new nuclei from vapour in the atmosphere, at least in the troposphere over oceans, is expected to be mainly the result of binary homogeneous nucleation of sulphuric acid/water droplets. Because of the strong attraction between sulphuric acid and water molecules, such nucleation is greatly enhanced over nucleation of the pure species. We shall describe some expressions proposed for the nucleation rate together with related experimental information, and observational information on nucleation in the atmosphere.

The nucleation rate J will depend on three variables which we take to be the vapour phase acid mass concentration c , the water relative humidity Rh , and the temperature T . The relative humidity Rh is the ratio of the water vapour pressure to its equilibrium value over a pure plane water surface and, taking the molecular weight of sulphuric acid to be 98.076, the mass concentration is related to the molecular concentration ρ , and the acid vapour pressure p_a by

$$\begin{aligned} c \text{ (}\mu\text{g m}^{-3}\text{)} &= 1.6286 \times 10^{-10} \rho \text{ (molecules cm}^{-3}\text{)} \\ &= 1.1796 \times 10^7 p_a \text{ (N m}^{-2}\text{)} / T \text{ (K)}. \end{aligned} \quad (12)$$

These relations are necessary in order to compare different proposed nucleation rates to each other. All authors and observations agree that J increases as c (or ρ or p_a) increase; as Rh increases; and as T decreases. Unfortunately, there is no such quantitative agreement between nucleation theories, or between theory and experiment as to the magnitude of J and its quantitative dependence on the variables, as we now show. The expressions we quote are based on classical binary nucleation theory applied to the sulphuric acid/water system (Jaeger-Voirol and Mirabel, 1989) which can be modified by the introduction of experimentally determined normalisation factors (Raes et al., 1992). It should be borne in mind, however, that classical theory totally fails to account for results for binary nucleation of water–alcohol systems (Viisanen et al., 1994).

Accurate experimental techniques have been developed to measure homogeneous nucleation rates (Strey et al., 1994), but it is difficult to apply these techniques to measure sulphuric acid/water nucleation rates and no results are available. The most comprehensive experiments available, which cover variations in all three

variables (with acid concentrations in terms of relative acidity Ra), were obtained by Wyslouzil et al. (1991) using a continuous flow mixing device. The results have not been parametrised for use in models, but they show a far greater sensitivity to temperature than rates calculated from classical nucleation theory, as shown in Fig. 11 of Wyslouzil et al. (1991). A temperature decrease of 5°C leads to an increase of 10^2 to 10^4 in the experimental nucleation rates.

We now review model parametrisations for nucleation rates based on classical theory and/or fits to various data. Although they cannot be relied on quantitatively for the reasons given above, they display the expected qualitative behaviour and have the advantage of ease of use in atmospheric modelling.

In their study of the relationship between dimethyl sulphide (DMS) flux and CCN concentrations in remote boundary regions, Pandis et al. (1994) used a rate based on homogeneous binary nucleation theory at 298 K (Jaeger-Voirol and Mirabel, 1989) enhanced by an experimentally determined factor of 10^7 (Raes et al., 1992):

$$\begin{aligned} \log_{10} J \text{ (cm}^{-3} \text{s}^{-1}\text{)} &= 7 + [- (64.24 + 4.7 Rh) \\ &+ (6.13 + 1.95 Rh) \log_{10} \rho] \end{aligned} \quad (13)$$

where ρ has units molecules cm^{-3} . In their recent review article on the dynamics of tropospheric aerosols, Pandis et al. (1995) give a formula for the critical sulphuric acid mass concentration corresponding to $J = 1 \text{ cm}^{-3} \text{ s}^{-1}$ for conditions in the lower troposphere:

$$\begin{aligned} c_{\text{crit}} \text{ (}\mu\text{g cm}^{-3}\text{)} &= 0.16 \exp(0.1 T - 3.5 Rh \\ &- 27.7). \end{aligned} \quad (14)$$

Easter and Peters (1994) in their study of nucleation and fluctuations quote a rate derived from fits to classical theory (Kreidenweis and Seinfeld, 1988) modified by a factor of 10^{-6} to account for hydrate effects (Jaeger-Voirol and Mirabel, 1988):

$$J = \alpha (Rh) S_a(T)^{\beta (Rh)} \quad (15)$$

where the saturation ratio for the acid, or relative acidity Ra , is

$$S_a(T) = p_a / p_{ae}(T). \quad (16)$$

The equilibrium vapour pressure is taken from Ayers et al. (1980):

$$p_{ae}(T) = 1.166 \times 10^{12} \exp(-10156/T) \text{ N m}^{-2}. \quad (17)$$

The parameters α and β take the values given in Table 2 (Easter and Peters, 1994).

Using Eq. (12), we can now compare the critical acid densities for $J = 1 \text{ cm}^{-3} \text{ s}^{-1}$ under various conditions given by Pandis et al. (1994) (only at 25°C), Pandis et al.

Table 2
Parameters for Eq. (15)

Relative humidity Rh	α (particles cm ⁻³ s ⁻¹)	β
0.1	1.57×10^{11}	12.3
0.5	3.86×10^{23}	10.0
1.0	1.45×10^{26}	8.04

(1995) and Easter and Peters (1994) (Eqs. (13)–(15)). The results are shown in Table 3. At the higher relative humidities and temperatures, critical densities from Pandis et al. (1995) and from Easter and Peters (1994) are close. The Easter and Peters (1994) formula gives a somewhat larger temperature variation, though not as large as found in the experiments of Wyslouzil et al. (1991). At low humidities, the much larger critical concentrations required by Easter and Peters (1994) would effectively preclude nucleation, compared to the Pandis et al. (1995) values, but this may not be important if nucleation is cut off anyway. The critical densities needed in the marine boundary layer study of Pandis et al. (1994) are small compared with the other values. If the nucleation factor of 10^7 in Eq. (13) is reduced to 10^4 (a sensitivity case considered by Pandis et al. (1994)) the densities in the final column in Table 3 would be increased to 0.646, 0.105 and 0.0177, respectively, bringing them within about a factor of 2 to the other values.

4.2. Fluctuations and nucleation

The rapid dependence of the nucleation rate on the variables c , Rh and T , together with experimental indications of even greater sensitivity to temperature than that suggested theoretically, means that fluctuations in conditions must play a major role in determining the location and magnitude of droplet nucleation in the atmosphere. This was investigated by Easter and Peters (1994) for

turbulence-scale fluctuations in temperature and water vapour concentration, treated as bivariate normal distributions with standard deviations of up to 1 K and 1 g kg⁻¹ about means of 288 K and 9.16 g kg⁻¹ (85% Rh), respectively. Considerable enhancement in nucleation rates was seen; the greatest enhancement occurring for a negative correlation between the variables. On the other hand, fluctuations resulting from diffusion from patches of warmer or colder water would produce a positive correlation between temperature and water content, and this may be the most likely circumstances in marine conditions. Observations at Swifterbrook in the Netherlands gave a positive correlation coefficient of 0.512 (Clement and Harrison, 1996) between the variables, which would indicate only a small increase of between 1.1 and 1.5 in the nucleation rate.

However, fluctuations in local aerosol concentrations as a result of rainfall near clouds, and localised acid production rates as a result of sunlight, are likely to have much more influence in driving nucleation events. In paper II we describe models for bursts of nucleation which could be produced by such fluctuations.

4.3. Observations of nucleation

Clarke (1992) has observed atmospheric nuclei with diameters greater than 3 nm in the remote free troposphere in 8–12 km altitude and between 70°N and 58°S. Regions with the highest number densities were generally found to have the lowest mass concentrations, and the particle densities appeared to be inversely related to the aerosol surface area available for condensation. The volatility of the particles suggests a sulphuric acid composition.

These observations are consistent with a process of intermittent homogeneous nucleation of sulphuric acid droplets and a history of air masses depicted in Fig. 2. For long periods of time, number concentrations fall while mass increases. The observations also show that

Table 3
Critical densities c_{crit} in $\mu\text{g m}^{-3}$ for homogeneous nucleation

Rh	T (°C)						
	0		12.5		25		
	Eq. (14) ^a	Eq. (15) ^b	Eq. (14)	Eq. (15)	Eq. (14)	Eq. (15)	Eq. (13) ^c
0.1	0.0756	0.432	0.251	2.106	0.921	8.97	0.154
0.5	0.0186	0.0154	0.0619	0.0750	0.227	0.320	0.0397
1.0	0.00329	0.00196	0.0108	0.00955	0.0395	0.0407	0.00755

^aPandis et al. (1995).

^bEaster and Peters (1994).

^cPandis et al. (1994).

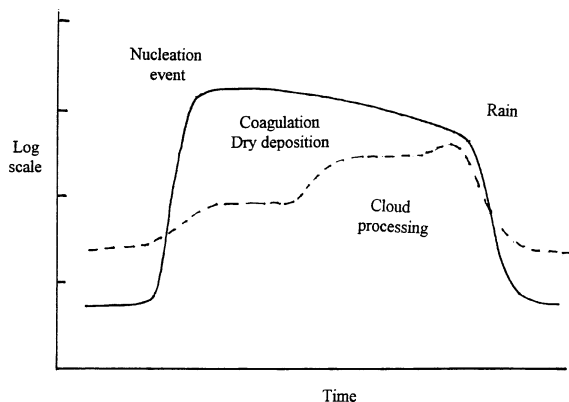


Fig. 2. History of an atmospheric air mass including nucleation, cloud processing and rainout, in terms of the aerosol number concentration (solid line) and mass concentration (dashed line).

instantaneous correlations between number and mass concentrations of aerosol cannot be used to deduce increases in number concentrations when extra sulphur is introduced into the atmosphere. If homogeneous nucleation is the dominant source of particles, it is only the frequency and character of these events which govern number concentrations, and the mass of aerosol during its evolution is irrelevant. For CCN production, however, increasing the mass as opposed to the number concentration can play a role in increasing the proportion of aerosol which is activated.

There have been several observations of particle formation in the marine boundary layer which can be attributed to nucleation events. Covert et al. (1992) observed rapid increases in particles greater than 3 nm in diameter following increases in SO_2 concentration. New particle formation in clean air near the Oregon coast was seen on numerous occasions by Hoppel et al. (1994), although the nucleation process could not be identified. Some nucleation events have been observed in the boundary layer over the Atlantic ocean (Van Dingenen et al., 1995). However, the failure of a model (Raes and Van Dingenen, 1992) to reproduce observed CCN concentrations in remote marine boundary layers, led Raes (1995) to suggest that many of these CCN have been entrained into the boundary layer from the free troposphere where they nucleate. Recently, nucleation events have been observed during the ACE-1 experiments in the Southern hemisphere (Weber et al., 1997), those at high altitudes being consistent with binary sulphuric acid/water nucleation. Hobbs (1993) has summarised observations of nucleation near clouds. Concentrations of nuclei in marine clouds and in halo regions surrounding the clouds have been found and they were much higher than in air well removed from the clouds. However, similar production in and around continental clouds has not been seen.

Therefore, nucleation in the free troposphere region seems to be intermittent and highly dependent on the amount of aerosol already present. This is consistent with homogeneous nucleation of sulphuric acid/water droplets. Near the sea, over continents, and in urban and rural regions where large SO_2 and other gas emissions occur, other mechanisms may contribute.

4.4. Alternative nucleation processes

Here, we briefly describe two alternative nucleation processes which are likely to occur. The question of their magnitude and whether they contribute significantly to nucleation in the atmosphere is not yet resolved.

Bursts of nanometre-size particles have been observed in Takhuse Observatory, situated in a sparsely populated rural region of Estonia (Horrak et al., 1995). Measurements of the air ion mobility spectrum during the day showed a population of charged ions with diameters increasing from 1 to 47 nm with time. This supports the hypothesis that there could be ion-induced nucleation in the atmosphere (Tammet et al., 1988).

Sources of ammonia exist over continents, and following reaction with sulphuric acid, clusters of ammonium sulphate molecules, possibly in association with water, are likely to be stable. The participation of ammonia in nucleation has been suggested by Weber et al. (1996), in order to interpret observations made in Hawaii (Weber et al., 1995, 1997). A particle nucleation rate proportional to the square of the acid molecular concentration, which is seen to be an approximation, suggests the absence of a nucleation barrier. Ammonium sulphate particles are assumed as the basis for the model of Jones et al. (1994) in their study of indirect radiative forcing by anthropogenic sulphate aerosols.

Theoretical work on multicomponent nucleation involving ammonia, sulphuric acid and water is not complete, and conditions when it would be barrierless are not known, but barrierless nucleation is an idealisation we can consider. When clusters are stable, classical nucleation theory is not appropriate because there is no free energy barrier. Instead, the rate of formation of large sizes is governed purely by kinematic factors and the monomer concentration. Theoretical methods exist for the solution of the corresponding growth equations (Goodrich, 1964; Clement and Wood, 1979; Blackman and Marshall, 1994; Lushnikov and Kulmala, 1995), but have not yet been applied directly to problems of aerosol formation in the atmosphere. We note that in continental atmospheric boundary layers, a wide variety of molecules and ions, some of them large, exist as stable or semi-stable species, and growth routes of observed atmospheric nuclei may well be more complicated than a treatment of a single species such as ammonium sulphate. Similarly, it is very unlikely that classical nucleation theory, even if it worked for a pure species, would be

adequate to describe nucleation rates in these boundary layers. In paper II we describe nucleation rates for species such as ammonium sulphate for which all clusters, including dimers, are stable.

5. Equilibration times for the Jaenicke aerosols

The competition between condensation on existing aerosol and new aerosol formation is governed by the evolution equation for the molecular concentration ρ of the condensable substance, which we may take to be sulphuric acid. Neglecting all transport terms, as these are not relevant to whether nucleation takes place, the equation is

$$d\rho/dt = P(t) - (\rho - \rho_e(T))R_A - R_N(\rho, T) \quad (18)$$

where $P(t)$ is the molecular production rate, and R_N is the molecular removal rate due to the formation and growth of the nucleated aerosol. The second term is the removal rate onto existing aerosol which is given by Eq. (6) or Eq. (8) integrated over the aerosol size distribution:

$$R_A = (1/\rho) \int n(R) J_v(R) dR = 4\pi D \int R F n(R) dR \quad (19)$$

where $F(Kn(R))$ is given by Eqs. (10) and (11). $\rho_e(T)$ is the equilibrium molecular concentration. The integrals can be expressed using moments M_n (Eq. (2)):

$$R_A(\text{continuum limit}) = 4 \pi D M_1 \quad (20)$$

$$R_A(\text{molecular limit}) = \pi S_p (8 kT/\pi M_a)^{1/2} M_2. \quad (21)$$

From Eq. (18), we see that the timescale for attaining equilibrium between the vapour and an individual aerosol component is

$$R_A^{-1} = 7958 M_1^{-1} s \quad (22)$$

$$= 1288 M_2^{-1} S_p^{-1} s, \quad (23)$$

for R_A given by Eqs. (20) and (21), respectively, at $T = 10^\circ\text{C}$ and for $M_a = 98.08 \text{ g}$ and $D = 10^{-5} \text{ m}^2 \text{ s}^{-1}$, corresponding to sulphuric acid molecules. We have evaluated R_A for the Jaenicke aerosols of Table 1, using M_1 or M_2 according to the size range of the lognormal distributions considered. Where there is an ambiguity, and the size range enters both continuum and molecular regions, a spread of values from choosing either M_1 or M_2 for a component is given in the results quoted in Table 4. We can then calculate the overall removal time-

Table 4
Moments and removal timescales for molecular deposition on aerosol

Aerosol	i	R (μm)	M_1 ($\mu\text{m cm}^{-3}$)	M_2 ($\mu\text{m}^2 \text{ cm}^{-3}$)	t_A	
					$S_p = 1$	$S_p = 0.02$
Polar	1	0.081	1.732 (1) ^a	0.194		
	2	0.476	0.089 (0.02)	0.068	73–103 min	19–65 h
	3	5.37	0.0016	0.014		
Background	1	0.011	1.399	0.138		
	2	0.150	8.986	1.900	3.7 min	4.9–35 min
	3	0.418	26.55 (0.02)	28.96		
Maritime	1	0.012	1.629	0.197		
	2	0.150	9.958	1.880	10.6 min	83 min–5.2 h
	3	0.439	1.345 (0.02)	1.359		
Remote continental	1	0.011	34.28	0.421		
	2	0.066	190.6 (1)	16.08	41–78 s	55–61 min
	3	1.32	0.396	1.124		
Desert dust storm	1	0.001	0.853	0.001		
	2	0.091	103.2 (1)	216.6	75 s	4.4 min
	3	17.96	3.198	159.1		
Rural	1	0.008	56.2	0.621		
	2	0.061	9.01 (1)	2.861	1.2–2 min	99 min
	3	0.051	100.6 (1)	7.389		
Urban	1	0.0076	757.9	7.94		
	2	0.023	25.61	6.22	0.2–15 s	12 min
	3	0.0034	1220 (1)	74.65		

^aThe numbers in brackets indicate the value of S_p in cases for which both M_i have been used to calculate the values of $t_A(S_p)$ obtained.

scale for each class of aerosol:

$$t_A = (\sum R_A(i))^{-1}. \quad (24)$$

We see that t_A is typically of the order of minutes. We shall look further into this data again in the next section, but first we comment on a likely solution to Eq. (18), discussed by Kerminen and Wexler (1995b). If R_N is negligible, which is the case if ρ is less than a critical value ρ_{crit} , and if t_A is much shorter than the timescale of changes in P , then

$$\rho - \rho_c(T) \approx P(t)/R_A = P(t) t_A. \quad (25)$$

When $P(t)$ is increasing ρ will increase until a ρ_{crit} is reached and nucleation commences. Eq. (25) will then no longer be valid. By correlating observed values of P and ρ using Eq. (25), t_A and therefore values of S_p can be obtained. The critical concentration can also be obtained, in principle, by noting the concentration at the beginning of a nucleation episode. The study of solutions to Eq. (18) during bursts of nucleation is continued in paper II.

6. Further characteristics of the Jaenicke aerosols

Different physical properties of atmospheric aerosols are specified by different moments of the size distribution.

We now examine in detail the moments of the individual components of the empirical aerosols of Jaenicke (1993). We are particularly interested in the connection between the moments and the gas-to-particle conversion process.

In Table 5 we present calculations of properties of the aerosol distributions of Table 1, which are now for convenience labelled P1, P2, P3, etc. The first column is the number n_i in each mode. The other columns arise from moments of the individual distributions: the mass concentrations c_i given by Eq. (4), the molecular removal rate specified by R_A (Eq. (20) or Eq. (21) as appropriate), and the mean aerosol radius given by Eq. (5). To calculate R_A for the molecular regime we have taken the sticking probability to be $S_p = 1$. In most cases it is clear which of Eqs. (20) and (21) is the best approximation for R_A . In a few cases the alternative results are close, but the resulting uncertainties in the values of R_A are not significant, and will not change the following observations and conclusions.

We study how the characterisation is related to the dynamical behaviour, in particular the effect of condensation represented by R_A . The data in Table 5 may be summarised as follows.

(i) As may be seen in the values of R_{av} , there is an obvious division into three modes:

Table 5
Characteristics of the Jaenicke aerosols

Aerosol	Label	n_i (cm^{-3})	c_i (g m^{-3})	R_A ($S_p = 1$) (s^{-1})	R_A ($S_p = 0.02$) (s^{-1})	R_{av} (μm)
Polar	P1	21.7	1.24×10^{-7}	1.51×10^{-4}	3.02×10^{-6}	0.08
	P2	0.186	3.52×10^{-7}	1.11×10^{-5}	1.06×10^{-6}	0.48
	P3	3.04×10^{-4}	7.58×10^{-7}	2.05×10^{-7}	2.05×10^{-7}	5.4
Background	B1	129	5.14×10^{-7}	1.07×10^{-4}	2.14×10^{-6}	0.01
	B2	59.7	2.36×10^{-6}	1.13×10^{-3}	2.95×10^{-5}	0.15
	B3	63.5	3.45×10^{-4}	3.34×10^{-3}	4.50×10^{-6}	0.42
Maritime	M1	133	9.71×10^{-7}	1.52×10^{-4}	3.04×10^{-6}	0.012
	M2	66.6	1.88×10^{-6}	1.25×10^{-3}	2.92×10^{-5}	0.15
	M3	3.06	1.32×10^{-5}	1.69×10^{-4}	2.11×10^{-6}	0.44
Remote continental	RC1	3200	1.29×10^{-8}	3.27×10^{-4}	6.55×10^{-6}	0.01
	RC2	2900	7.30×10^{-6}	1.25×10^{-2}	2.50×10^{-4}	0.066
	RC3	0.3	2.78×10^{-5}	4.98×10^{-5}	1.75×10^{-5}	1.32
Desert dust storm	D1	726	1.31×10^{-11}	1.08×10^{-6}	2.16×10^{-8}	0.001
	D2	1140	4.42×10^{-2}	1.30×10^{-2}	3.36×10^{-3}	0.09
	D3	0.178	9.17×10^{-2}	4.02×10^{-4}	4.02×10^{-4}	18
Rural	R1	6650	3.76×10^{-8}	4.82×10^{-4}	9.65×10^{-6}	0.008
	R2	147	1.98×10^{-5}	1.32×10^{-3}	4.45×10^{-5}	0.061
	R3	1990	3.31×10^{-6}	5.74×10^{-3}	1.15×10^{-4}	0.05
Urban	U1	99300	4.80×10^{-7}	6.18×10^{-3}	1.24×10^{-4}	0.0076
	U2	1110	6.63×10^{-5}	4.83×10^{-3}	9.67×10^{-5}	0.023
	U3	36400	3.50×10^{-5}	5.80×10^{-2}	1.16×10^{-3}	0.034

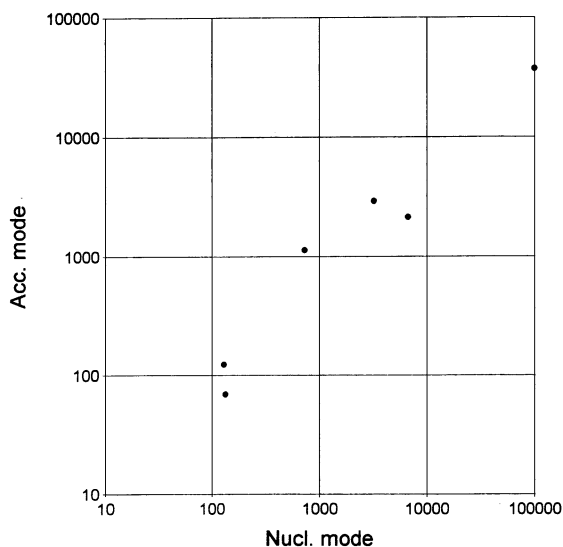


Fig. 3. Apparent correlation between atmospheric aerosol number concentration in the accumulation mode (cm^{-3}) and the number concentration in the nucleation mode (cm^{-3}).

Nucleation mode ($R_{av} \leq 0.01 \mu\text{m}$); members B1, M1, RC1, D1, R1, U1

Accumulation mode ($0.01 < R_{av} < 1 \mu\text{m}$); members P1, P2, B2, B3, M2, M3, RC2, D2, R2, R3, U2, U3

Giant particles ($R_{av} > 1 \mu\text{m}$); members P3, RC3, D3

- (ii) There is no separate nucleation mode for the polar aerosol, but those in the other regions all contain nucleation and accumulation mode components. In Fig. 3 the total number concentrations in the two modes are plotted against each other. They are remarkably close to being equal over a range of three orders of magnitude in different parts of the atmosphere. The universality of this result needs to be investigated further for typical global aerosols, and if verified, requires a dynamical explanation.
- (iii) Except for the rural and urban regions, the mass concentration of the aerosols is dominated by the largest size component. In the rural and urban regions the intermediate size components provide the largest mass concentrations because of their wide size ranges.
- (iv) Vapour removal rates are controlled by accumulation mode components in every case, though this is the smallest size component for the polar aerosol. Contributions to R_A from the nucleation mode are never more than 10% of the total. Contributions from the three giant particle modes are even smaller and can be neglected.
- (v) On changing S_p from 1 to 0.02, the fluxes onto the giant size aerosols hardly change as they are limited

by diffusion, whereas those onto the very small aerosols are reduced by a factor of 50. Qualitatively, the largest fluxes are directed onto the accumulation mode aerosols, as previously noted by Kerminen and Wexler (1995b).

These properties, on which we base the following conclusions, have far reaching consequences, and their veracity and generality need further tests against observation. The other dynamical property to bear in mind is that the molecular concentration of a substance in the atmosphere will generally be specified by its production rate divided by R_A unless nucleation is taking place (Eq. (25)), and only when it reaches a critical value will nucleation occur. This and the empirical properties deduced from the Jaenicke aerosols enable us to make the following conclusions:

1. The giant size dust and other entrained aerosols play no significant role in the dynamics of aerosol nucleation and growth in the atmosphere. Because of their small number concentrations, it is also likely that they have no significance in coagulation processes. This leads to the following two conclusions.

2. Since the giant size can dominate the aerosol mass, the mass is not a controlling factor in aerosol dynamics in the atmosphere and need not be calculated in atmospheric aerosol modelling, at least as far as gas-to-particle conversion is concerned.

3. A similar conclusion applies to large size dusts which produced from continents, especially deserts. The input and presence of such an aerosol is not necessary in a global aerosol model which seeks to describe the gas-to-particle conversion process.

4. The fact that the nucleation mode does not provide the main vapour removal sink for these average aerosols implies that nucleation is not normally taking place. This suggests that nucleation will only take place intermittently, i.e. when the molecular production rate is high enough, and existing aerosol only provides a small removal rate, so that the vapour concentration is large enough for nucleation to occur. This particularly applies to homogeneous nucleation which is extremely sensitive to the molecular concentration. This picture is consistent if we view nucleation as a self-terminating burst process. This is the key process for new particle production in the atmosphere and most of paper II is devoted to its detailed examination.

5. Nucleation mode removal is much more significant in the rural and urban atmospheres than in the rest of the atmosphere, reaching up to 10% of accumulation mode removal. This suggests that nucleation is much more frequent in urban and rural environments, a conclusion which is obviously in accordance with larger gas phase production of involatiles and the much larger aerosol number concentrations observed.

6. Since aerosol formation and aerosol removal which is mainly associated with precipitation, are processes which both have short timescales compared to aerosol lifetimes in the atmosphere, a realistic model of the atmosphere must represent these, and the resulting time-dependent fluctuations in aerosol content. Average removal rates, such as those used in the model of Langner and Rodhe (1991) are not adequate: precipitation removal must be treated either deterministically or by a stochastic model. These conclusions are similar to those reached by Kerminen and Wexler (1995a, b).

7. The nucleation and accumulation modes will have different dynamical behaviour. For example, coagulation is important for the nucleation mode, whereas it is often neglected between particles in the accumulation mode, although coagulation with particles in the nucleation mode are included. Some accumulation mode aerosol will be incorporated into clouds as CCN. These points are discussed in detail by Kerminen and Wexler (1995a).

A minimum requirement for a realistic atmospheric aerosol model is therefore the use of two modes, but a proper representation of the interaction of the aerosol with clouds may require an additional mode. Aerosol acting as CCN can grow considerably from chemical processes in droplets, leaving larger particles following droplet evaporation and these are then more likely to be removed by precipitation. Three modes are used in the model of Wilson and Raes (1996): the third mode is defined for particles larger than the critical diameter for activation at 0.2% supersaturation.

7. Conclusions

An understanding of the formation and evolution of atmospheric aerosols are important for quantifying their effect on the climate. Coagulation and removal mechanisms, reviewed by Pandis et al. (1995) and Hobbs (1993), are much better understood than the formation mechanisms through gas-to-particle conversion. The competition between nucleation and growth determines the increase in the number concentration of the atmospheric aerosol when more vapour is added to the atmosphere, and therefore the increase in scattering of solar radiation and the number of CCN. As recognised by Kerminen and Wexler (1995b), the key equation which determines the result of this competition describes the evolution of the concentration of the condensable molecules. This contains removal rates for condensation on existing aerosol and a possible additional term for nucleation. In this paper, we have reviewed the ingredients of these two terms, principally for sulphuric acid molecules. We have also looked at empirical data on atmospheric aerosols to determine the magnitude of the removal terms.

There is no doubt that the vast majority of particles found in the atmosphere are produced by nucleation from the vapour phase. Furthermore, the much larger concentrations found in urban air masses indicate that anthropogenic gas emissions increase the concentration of particles in the atmosphere. We have identified several difficulties, but also several avenues of research for quantifying the relation between SO₂ emissions into the atmosphere and consequent increases in aerosol number concentrations needed by climate models (Langner and Rodhe, 1991; Jones et al., 1994). Our conclusions are the following.

1. Molecular removal rate onto aerosol: This will often specify the molecular concentration in the atmosphere (through Eq. (25)). For sulphuric acid molecules there is a large difference in removal rates used at present arising from differing values for the molecular sticking probability. For theoretical reasons we favour a value of unity, which is the value supported by experiments on other molecules such as water.

2. Nucleation in the atmosphere: Good evidence exists that in marine environments and in the free troposphere, nucleation takes place in intermittent events specified by low temperature, high humidity, and low aerosol mass concentration. This is consistent with the homogeneous nucleation of sulphuric acid/water droplets, a mechanism which several authors believe also occurs elsewhere in the atmosphere.

3. Nucleation over continents and near sources of ammonia: Although sulphuric acid/water nucleation may take place in some circumstances, such as in plumes, there is also evidence of ion-induced nucleation. There also exists the possibility of nucleation of involatile species produced by chemical reaction, such as ammonium sulphate. Such nucleation perhaps has no free energy barrier, in which case its rate is much less concentration dependent than are homogeneous nucleation rates.

4. Various parametrisations of the results of classical binary nucleation theory for sulphuric acid/water nucleation are fairly consistent with each other, exhibit the correct trends with parameter changes (acid concentration, relative humidity, and temperature), but show major differences compared with available experimental data, which have in particular a stronger temperature dependence.

5. Fluctuations in atmospheric aerosol concentrations, partly arising from rapid removal of aerosol mass by precipitation, play a major role in nucleation. The consequent evolution of aerosol mass and number concentration can explain the negative correlation between the two variables observed in the free troposphere. It is characteristic of infrequent bursts of nucleation.

6. The analysis of the empirical aerosols of Jaenicke (1993) leads to interesting conclusions which need further observational verification and explanation. We find

a correlation between number concentrations in the nucleation and accumulation modes; that giant particles and the aerosol mass are not relevant to the gas-to-particle conversion process; and that nucleation is less intermittent in urban and rural environments than in the remote atmosphere. The intermittency of nucleation and the importance of fluctuations have also been emphasized by Easter and Peters (1994) and Kerminen and Wexler (1995b).

To conclude, only in rare localised regions, such as some marine boundary layers, steady-state aerosol concentration is possible. Realistic models of atmospheric aerosol must follow the time-dependent behaviour of the aerosol from nucleation bursts to precipitation events which remove sufficient aerosol for nucleation to re-occur. When P , the input of condensable molecules to the atmosphere increases, the removal rate to the aerosol will increase and so will the aerosol mass before it is removed by precipitation. Once the aerosol starts to nucleate, the number of particles produced is expected to increase as P increases: this is studied in paper II. In urban areas, and where other involatile species can be produced (forests and sources of ammonia), the increase may depend on nucleation mechanisms other than homogeneous nucleation, which continue to produce new particles even when there is a large increase in existing aerosol mass and the vapour removal rate.

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