



## Gas-to-particle conversion in the atmosphere: II. Analytical models of nucleation bursts

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### Abstract

Simple models are developed to describe the formation of particles from condensable vapours in different atmospheric circumstances. The models are designed for use in large scale global transport models, where sub-grid descriptions are required for such phenomena. We solve the evolution equation for the density of a condensable vapour. When the concentration of existing aerosol is low, nucleation can occur, but only in intermittent, isolated bursts. In the absence of an initial aerosol, two analytical expressions are obtained for the number of particles produced in such bursts, valid for high and low rates of vapour production, respectively. These results compare favourably with calculations made using a detailed numerical code, using the homogeneous nucleation of sulphuric acid/water droplets as an illustration. Then we consider barrierless nucleation, where clusters are always stable against evaporation, which is relevant to the production of ammonium sulphate particles in the atmosphere. We go on to consider conditions where existing aerosol can affect the production of particles, and also consider slower bursts where the time dependence of the vapour production rate, and not condensation on the nucleated aerosol, cuts off nucleation. © 1998 Elsevier Science Ltd. All rights reserved.

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### Nomenclature

$\alpha$	from Eq. (9)
$\eta$	from Eq. (4)
$\beta$	exponent in nucleation rate
$\mu$	from Eq. (8)
$\lambda$	mean free path
$\rho$	vapour molecular density
$\rho_m$	maximum vapour density
$\rho_d$	droplet mass density
$\omega$	frequency for production rate

$D$	diffusion coefficient
$k$	Boltzmann's constant
$p_s$	vapour pressure at surface
$S_p$	sticking probability
$G$	droplet growth rate
$X_a$	acid mole fraction
$J$	nucleation rate
$n$	aerosol size distribution
$S$	vapour supersaturation
$c_1$	monomer density
$\alpha_1$	monomer–monomer collision rate
Rh	relative humidity
$t, t', t''$	time
$P$	molecular production rate
$T$	temperature

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$R$	droplet radius
$R_A$	removal strength on existing aerosol
$R_N$	removal rate on nucleated aerosol
$t_m$	time at peak of burst
$t_c$	timescale for burst
$J_v$	molecular deposition rate on droplet
$p_a$	sulphuric acid vapour pressure
$p_{ae}$	equilibrium acid vapour pressure
$K_n$	Knudsen number
$M_a$	sulphuric acid molecular mass
$M_w$	water molecular mass
$X_w$	water mole fraction
$J_0$	nucleation rate prefactor
$R_{min}$	initial size of nucleated particles
$N$	number density of particles nucleated
$t_A$	timescale for removal on existing aerosol
$\alpha_g$	from Eq. (34)

## 1. Introduction

Gas-to-particle conversion in the atmosphere can be of two forms: either the growth of an existing aerosol or the nucleation of new particles. Observational evidence for the relative importance of these processes has been reviewed in a companion paper, to be referred to as paper I (Clement and Ford, 1998). It seems clear that condensation on an existing aerosol is more likely on average, so that particle production in the atmosphere takes place only in occasional and isolated bursts of nucleation. The main purpose of this paper is to develop analytical models to predict the number of particles produced in such bursts.

Nucleation events are brought about by the build-up of the concentration of condensable vapour in the atmosphere, either generated in situ by various chemical reactions, or brought in from distant sources by transport processes. The dependence of the particle yield on the production rate of condensable molecules is of particular interest, since it relates the likely increase in atmospheric aerosol concentrations to the increase in the emissions of gas phase precursors, such as  $\text{SO}_2$ . The input of aerosol into the atmosphere is an important aspect of the modelling of global atmospheric aerosols, and which in turn plays a role in estimating climate change effects due to human activity (Jones et al., 1994).

As was shown in paper I, the evolution of the molecular concentration of condensable species in the atmosphere is of central importance. The equation which determines this evolution contains a molecular production rate; and the key terms of removal of material onto existing aerosol; and removal by the nucleation and growth of new particles. This competition in removal has been considered before (Friedlander, 1978), often numerically (McGraw and Saunders, 1984). In some circum-

stances, particularly in the absence of existing aerosol, the rapid growth of freshly nucleated aerosol can be strong enough to deplete the molecular concentration and cut off the nucleation process, terminating the nucleation burst. Alternatively, nucleation can simply follow the molecular production rate, or occur at a negligible rate if the existing aerosol is a stronger sink for vapour. However, in most cases it is unreasonable to expect a large scale atmospheric model to treat nucleation bursts explicitly, since they will often occur on very short timescales, and would slow down the code unacceptably. Analytical approximations for burst dynamics governed by the evolution equation will therefore be valuable as the basis of sub-grid models in such codes.

The binary homogeneous nucleation of sulphuric acid–water droplets may dominate in regions such as the free troposphere. However, this is not the only possible nucleation process. Where ammonia is present, it is possible to form ammonium sulphate molecules or clusters formed from sulphuric acid, ammonia and water molecules. There have been reports of observations of nucleation events proportional to the square of acid concentration (Weber et al., 1996), and this suggests that sticking together of two acid molecules leads to nucleation. To describe this mechanism we consider the idealisation of “barrierless nucleation”, where all clusters of molecules are considered to be stable, unlike normal homogeneous nucleation, which is governed by the probability of forming a critical cluster against the trend of cluster decay.

Models of these processes will be developed here according to the following plan. In Section 2 we consider homogeneous nucleation of sulphuric acid/water droplets. The temperature is taken to be constant and the dynamics are driven solely by vapour production and removal. The case where nucleation is driven by changes in temperature is to be described elsewhere (Ford and Clement, 1998). The analytic treatments of Barrett and Clement (1991) and Barrett (1992) are extended to obtain the number of nuclei produced by a burst in terms of the molecular production rate of gas phase sulphuric acid. Results are obtained according to whether or not significant growth of nuclei takes place during the nucleation pulse. An earlier theory developed by Shaw (1989) corresponds to the case when growth is significant, whereas some bursts are too fast to allow much growth. In Section 2.3 we compare the analytical results with those of a numerical code describing the burst process. The accuracy of the approximations made are examined in Appendix A. In Section 2.4 we briefly survey the problems of relating burst models to global model grid scales.

The theory of Lushkinov and Kulmala (1995) is extended in Section 3 to describe barrierless nucleation, and in particular to illustrate conditions where condensation on existing aerosol as well as on freshly nucleated droplets should be taken into account. We calculate the

time required for the removal rate onto the freshly nucleated aerosol to equal the molecular production rate, and compare this with the timescale for vapour removal onto existing aerosol. This allows us to estimate the effect of a competition between nucleation and condensation on an existing aerosol for this mechanism. In Appendix B we present a similar analysis for homogeneous nucleation. Whilst most numerical results in this paper are obtained under the assumption that molecular sticking probabilities for condensation are equal to unity (Clement et al., 1996), at the end of Section 3 we also consider the effect of a large reduction in its value. Our conclusions are given in Section 4.

The case of a nucleation burst terminated by a time-dependent molecular production rate effect and not by the growth of fresh nuclei is considered in Appendix C. A simple expression is obtained for the total number of nuclei produced in such a “slow” source-limited burst of nucleation. A nomenclature is provided in Appendix D.

## 2. Homogeneous nucleation

Homogeneous nucleation is characterised by a free energy barrier inhibiting cluster formation, and by a very rapid rise in the rate of particle formation with molecular concentration. Binary homogeneous nucleation of sulphuric acid/water droplets is the example we consider here.

We start with the general equation for the evolution of the molecular concentration of a condensable species  $\rho$ :

$$d\rho/dt = P(t) - (\rho - \rho_e(T))R_A - R_N(\rho, \rho_{\text{crit}}, T) \quad (1)$$

where  $P(t)$  is the production rate in molecules per  $m^3$  per second. The second term is the removal rate onto existing (accumulation mode) aerosol, which is linear in the difference between  $\rho$  and  $\rho_e(T)$ , the equilibrium concentration at the temperature  $T$ .  $R_A$  is the removal strength for this process, and  $R_N$  is the removal rate onto nucleated droplets, which is negligible unless  $\rho$  exceeds a critical value  $\rho_{\text{crit}}$ . This equation has also been considered by Wilson and Raes (1996).

Changes with time in  $P(t)$  and  $R_A$  are normally slow, but rapid changes in vapour concentration take place if nucleation occurs. The number of droplets produced by a burst of nucleation, starting from a fixed initial vapour concentration, was estimated analytically by Barrett and Clement (1991) and modifications necessary to take into account a molecular production rate and condensation on existing aerosol were examined by Barrett (1992). Here, we extend this theory and apply it to the case of homogeneous binary nucleation of sulphuric acid/water droplets. We first need simple forms for the aerosol nucleation and growth rates.

### 2.1. Aerosol growth rate and nucleation rate

The sulphuric acid molecular deposition rate onto a spherical droplet of radius  $R$  is

$$J_v = 4\pi R F(R) D (p_a - p_s) / kT \quad (2)$$

where  $D$  is the vapour diffusion coefficient,  $k$  is Boltzmann's constant,  $p_a$  is the acid vapour pressure and  $p_s$  is the vapour pressure at the droplet surface, which is given by its equilibrium value  $p_{ae}(T)$  at the ambient temperature  $T$ , multiplied by the acid activity in the condensed phase.  $F(R)$  is the modified Fuchs-Sutugin factor which extends the growth rate from the continuum regime into the transition regime and which is specified by the Knudsen number  $K_n$ :

$$F(R) = f(K_n) / (1 + 1.33 K_n f(K_n) [1/S_p - 1]) \\ f(K_n) = (1 + K_n) / (1 + 1.71 K_n + 1.33 K_n^2) \quad (3)$$

Here,  $K_n = \lambda/R$ ,  $S_p$  is the molecular sticking probability; and  $\lambda$  is the molecular mean free path in air. We define  $\lambda = 0.75D (2\pi M_a/kT)^{1/2}$  to give the correct limit for large  $K_n$ .

We also need to consider water vapour deposition on the droplet. This is assumed to proceed rapidly to maintain a molar ratio of water and sulphuric acid in the condensed phase consistent with the given gas phase activities. The growth rate  $G = dR/dt$  is given by  $G = \eta M_a J_v / (4\pi R^2 \rho_d)$  where  $\rho_d$  is the droplet density, with

$$\eta = (M_a X_a + M_w X_w) / M_a X_a \quad (4)$$

where  $M_a$  and  $M_w$  are the molecular masses, and  $X_a$  and  $X_w$  are the condensed phase mole fractions for acid and water molecules, respectively.

We also assume that the equilibrium acid concentration over the mixed droplet is negligible so that the decay term containing  $p_s$  in Eq. (2) can be ignored. Decay plays a role in nucleation, though, and we use a simple expression for the nucleation rate (Easter and Peters, 1994) which is a function of the saturation ratio or relative acidity  $S = p_a/p_{ae}(T)$ , where the equilibrium pressure is (Ayers et al., 1980):

$$p_{ae}(T) = 1.166 \times 10^{12} \exp(-10156/T) N m^{-2}. \quad (5)$$

The growth rate now becomes

$$G = [(M_a X_a + M_w X_w) / X_a] (\rho(t) / \rho_d) \{ (R/D) \\ \times [1 - 0.62 K_n / (1 + K_n)] + (2\pi M_a / kT)^{1/2} / S_p \}. \quad (6)$$

The continuum ( $K_n \rightarrow 0$ ) and molecular ( $K_n \rightarrow \infty$ ) limits emerge when the first and last terms, respectively, dominate in the curly brackets. However, if the sticking probability  $S_p$  is small, the term proportional to  $0.62 K_n / (1 + K_n)$  has little effect because the last term still

dominates even for  $K_n = 1$ . We shall neglect it to obtain the simple form used by Barrett and Clement (1991) to treat bursts of nucleation analytically. We use

$$G = \eta\mu M_a \rho(t)/(1 + \alpha R) \tag{7}$$

where

$$\mu = S_p(kT/2\pi M_a)^{1/2}/\rho_d \tag{8}$$

$$\alpha = (S_p/D) (kT/2\pi M_a)^{1/2}. \tag{9}$$

The acid removal rate onto existing aerosol is given by

$$R_A = (1/\rho) \int n(R) J_v(R) dR = 4\pi\mu\rho_d \int n(R) R^2/(1 + \alpha R) dR, \tag{10}$$

where  $n(R)$  denotes the size distribution of the existing aerosol. Clement (1978) describes how this rate can be calculated in terms of an initial size distribution  $n(R)$ .

2.2. Burst of nucleation model

During a burst of nucleation of sulphuric acid/water droplets in the atmosphere we expect a new nucleation mode aerosol to be formed, while removal of molecules onto an accumulation mode aerosol continues. The aerosol size distribution can be written as

$$n(R, t) = n_c(R, t) + n_A(R, t). \tag{11}$$

Eq. (1) for the vapour molecular concentration is now

$$d\rho/dt = P(t) - \rho R_A(t) - R_N(\rho, \rho_{crit}, T). \tag{12}$$

By analogy with Eq. (10), the nucleation mode removal rate is

$$R_N(\rho, \rho_{crit}, T) = 4\pi\mu\rho_d \int_{R_{min}} n_c(R) R^2 dR \tag{13}$$

since the  $\alpha R$  term is negligible.  $R_{min}$  is the critical size at which particles are nucleated. This integral is now evaluated using a substitution (Barrett and Clement, 1991) which relates the size distribution  $n_c$  at time  $t$  to a nucleation rate at an earlier time  $t'$ :

$$n_c(R, t) = -(\partial t'/\partial R) J(\rho(t')), \tag{14}$$

where  $J$  is the rate of nucleation, per unit volume, of nuclei of size  $R_{min}$  at time  $t'$  when the acid concentration is  $\rho(t')$ . Note that  $t'$  can be considered to be a function of  $t$  and  $R$ . Then

$$R_N(t) = 4\pi\mu\rho_d \int_0^t J(\rho(t')) R^2(t, t') dt' \tag{15}$$

The trajectory for radial growth in the interval from  $t'$  to  $t$  is

$$\begin{aligned} R(t, t') &= \eta M_a \mu \int_{t'}^t dt'' \rho(t'') \\ &= R_{min} + \eta M_a \mu (y(t) - y(t')) \end{aligned} \tag{16}$$

where  $dy/dt = \rho(t)$ .

We assume that if significant nucleation occurs, it is cut off by growth of freshly nucleated aerosol and not by growth on the existing aerosol. This must be the case if the accumulation mode removal timescale

$$t_A = R_A^{-1}, \tag{17}$$

is short compared with the timescale for change in  $P(t)$ . The alternative possibility, to be discussed in Appendix C, is that the nucleation timescale is determined by  $P(t)$ .

For convenience, we choose the rate of binary homogeneous nucleation of sulphuric acid/water droplets to be given by

$$J = J_0(\text{Rh}, T) \rho^{\beta(\text{Rh})}, \tag{18}$$

where Rh is the relative humidity and  $J_0$  is a prefactor. Since the exponent  $\beta$  lies in the range 8–12 for typical conditions (Easter and Peters, 1994), the nucleation rate is a very rapidly varying function, and we adapt the procedure of Barrett (1992) to determine the results of a nucleation burst. The vapour density  $\rho$  will have a maximum at a value  $\rho_m$  at time  $t_m$ , and the nucleation rate  $J$  can be expanded about its very sharp maximum at this point. This is the key step in the analysis

$$\rho = \rho_m + \frac{1}{2}\rho''_m (t - t_m)^2 \tag{19}$$

where  $\rho''_m$  is the second derivative of  $\rho$  with respect to time, evaluated at  $t_m$ . So

$$\begin{aligned} J(\rho(t)) &= J(\rho_m) [1 + \frac{1}{2}\rho''_m (t - t_m)^2/\rho_m]^\beta \\ &\approx J(\rho_m) \exp[\frac{1}{2}\beta\rho''_m (t - t_m)^2/\rho_m]. \end{aligned} \tag{20}$$

Note that  $\rho''_m$  is negative. Near the peak, we evaluate the function  $y$ :

$$\begin{aligned} y(t) - y(t') &= \rho_m(t - t') \\ &+ \rho''_m [(t - t_m)^3 - (t' - t_m)^3]/6. \end{aligned} \tag{21}$$

We are now in a position to determine the maximum in  $\rho$  approximately from Eq. (12). At the peak  $d\rho/dt$  vanishes so that

$$\begin{aligned} P(t_m) &= \rho_m R_A(t_m) + 4\pi\mu\rho_d \rho_m \int_0^t m J(\rho(t')) R^2(t_m, t') dt' \\ &= \rho_m R_A(t_m) + \eta^2 \mu^3 M_a^2 \rho_d \rho_m^3 J(\rho_m) (-2\pi\rho_m/\beta\rho''_m)^{3/2} \end{aligned} \tag{22}$$

where the integral has been evaluated using Eqs. (16), (20) and (21), keeping only the leading term for  $y$ , and extending the lower limit of integration to  $-\infty$ . Terms involving  $R_{min}$  have been neglected.

We can also find  $\rho''_m$  by differentiating Eq. (12):

$$\begin{aligned} \rho''_m &= dP(t_m)/dt - \rho_m dR_A(t_m)/dt - 4\pi\mu\rho_d \rho_m [J(t_m) R_{min}^2 \\ &+ \int_0^{t_m} J(\rho(t')) 2R(t_m, t') \partial R(t = t_m, t')/\partial t dt']. \end{aligned} \tag{23}$$

From equation (16),  $\partial R(t = t_m, t')/\partial t = \eta\mu M_a \rho_m$ , and the integral is then evaluated as before. Again, we neglect all the small terms involving  $R_{\min}$  and also the term involving  $dR_A(t_m)/dt$ . The result is

$$\rho_m'' = dP(t_m)/dt - 4\eta^2\mu^3 M_a^2 \rho_d \rho_m^3 J(\rho_m) \times (-2\pi\rho_m/\beta\rho_m''). \tag{24}$$

The total number of nuclei  $N$  produced by the burst is obtained by integrating  $J(\rho(t))$  given by Eq. (20) over all time:

$$N = J(\rho_m) (-2\pi\rho_m/\beta\rho_m'')^{1/2}. \tag{25}$$

Eqs. (22), (24) and (25) involving  $\rho_m''$  and  $\rho_m$  must be supplemented by an equation for  $t_m$  in order to determine  $P(t_m)$  and its derivative. One approach is to use the approximate Eq. (20) for  $J$  to determine  $t_m$ . This gives

$$t_m = \{(-2\rho_m/\beta\rho_m'')\ln[J(\rho_m)/J(\rho_{\text{crit}})]\}^{1/2} \tag{26}$$

if  $\rho = \rho_{\text{crit}}$  at  $t = 0$ . The nucleation time period  $t_c$  can be defined as the time during which the rate is within a factor  $e$  of its maximum value. This will be equal to twice  $t_m$  in Eq. (26) when  $J(\rho_m) = eJ(\rho_{\text{crit}})$ :

$$t_c = 2(-2\rho_m/\beta\rho_m'')^{1/2}. \tag{27}$$

Alternatively, we can simply consider conditions where  $P$  is a constant during the burst and so its derivative can be ignored. This situation would be appropriate for bursts which are short on the timescale of changes in  $P$ . This simplification is made from now on, and relaxed in Appendix C.

Taking Eqs. (22), (24) and (25), and ignoring the time dependence of  $P$  during the burst, it is possible to eliminate the unknown quantities  $\rho_m$  and  $\rho_m''$  and derive an expression for  $N$ . We also ignore vapour condensation onto existing aerosol. The number of particles nucleated is

$$N = (\pi J_0^3 / (2\beta\mu^3 \rho_d \eta^2 M_a^2))^{1/4} (8\beta^3 P^4 / (\eta^2 M_a^2 \mu^3 \pi^3 J_0 \rho_d))^{(3\beta - 2)/(4(\beta + 6))}. \tag{28}$$

This result demonstrates the reduction in sensitivity to the details of the nucleation rate brought about by the termination of the burst by vapour depletion. The exponent of the acid saturation ratio in the nucleation rate,  $\beta$  in Eq. (18), is approximately 10 reflecting the sensitivity of homogeneous nucleation theory to the vapour concentration. However, this translates in Eq. (28) into a variation in  $N$  with vapour source rate  $P$  according to a exponent  $\alpha = (3\beta - 2)/(\beta + 6)$ . This is equal to 1.75 for  $\beta = 10$ , and varies little as  $\beta$  is changed. Similarly,  $N$  is proportional to the prefactor  $J_0$  in the nucleation rate raised to the power  $5/(\beta + 6)$ . For  $\beta = 10$ , this is only 0.3125. Three orders of magnitude uncertainty in the numerical value of  $J_0$  translate into one order of magnitude of uncertainty in  $N$ .

The above results are similar to those derived by Shaw (1989) who considered a similar dynamical equation for a condensable vapour during a nucleation burst, but who made different approximations for its solution. He found the time at which the nucleation and growth vapour sink strengths were equal, and integrated the equation up to that point.

We make a new development of the model starting again from Eq. (16) but this time neglecting the final term instead of the initial nucleation size. This approximation would apply for rapid bursts (on the timescale of droplet growth) during which the nucleated droplets do not change their radius significantly.  $R_{\min}$  is typically about a nanometre. Eq. (25) is unchanged, but Eqs. (22) and (24) become, respectively,

$$P(t_m) = 2\pi\mu\rho_d\rho_m N R_{\min}^2 \tag{29}$$

and

$$\rho_m'' = -4\pi\mu\rho_d\rho_m J_0 \rho_m^\beta R_{\min}^2 \tag{30}$$

and the result for  $N$  is just

$$N = (J_0 / (2\beta\mu\rho_d R_{\min}^2))^{1/(2+\beta)} (P / 2\pi\mu\rho_d R_{\min}^2)^{\beta/(\beta+2)} \tag{31}$$

which shows the same reduced sensitivity to the details of the nucleation rate. This time,  $N$  is proportional to  $P$  to the power 0.833 for  $\beta = 10$ , and the dependence on  $J_0$  is through an exponent of only 1/12.

### 2.3. Numerical calculations

Some example calculations of a burst of nucleation of sulphuric acid/water droplets have been performed using a numerical code which evolves an assumed log-normal size distribution, taking into account nucleation and competing condensation. The code is based on the work of Pratsinis (1988), and for ease of comparison with the analytical model predictions, contains Eq. (18) to represent the nucleation rate. However, the size of the new nuclei are calculated from the classical theory of binary homogeneous nucleation. The temperature and molecular source rates are chosen to be typical for atmospheric conditions, and the simulations start with no existing aerosol, corresponding to a nucleation burst in the atmosphere following the removal of aerosol, for example by rainfall. This is the most efficient scenario for particle production.

Fig. 1 illustrates how both the acid concentration and nucleation go through maxima, and also shows the integrated number of new particles produced. The conditions are  $P = 10^{11}$  molecules of acid generated  $\text{m}^{-3} \text{s}^{-1}$ , and a relative humidity Rh of 0.5 at  $T = 273$  K. In Fig. 2, the square symbols are the calculated numbers of particles nucleated for different rates of acid production, according to the numerical code. The solid line is the prediction

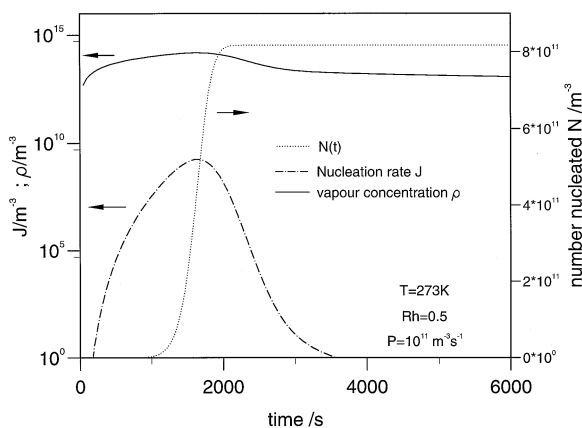


Fig. 1. Evolution of sulphuric acid molecular concentration  $\rho$  and aerosol number density  $N$  with time through a burst of nucleation driven by an acid production rate of  $10^{11}$  molecules  $\text{m}^{-3} \text{s}^{-1}$ , and at a relative humidity  $R_h$  of 0.5 at 273 K. The behaviour is calculated numerically using a log-normal aerosol evolution code. The time dependence of the nucleation rate  $J$  is also shown.

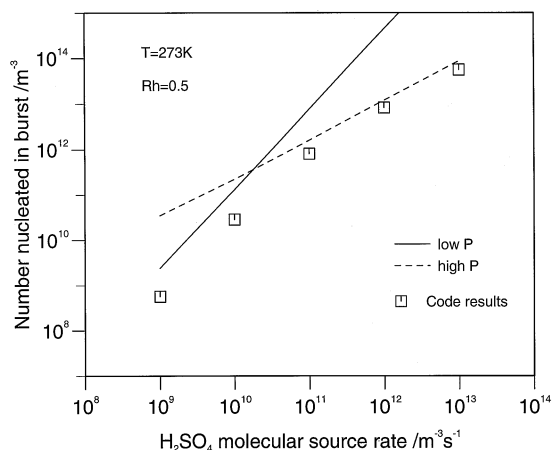


Fig. 2. Dependence of the number density  $N$  of particles nucleated for a production rate of sulphuric acid molecules  $P$ , according to the numerical code at 273 K and  $R_h = 0.5$ . The dependence of  $N$  upon  $P$  is compared with the predictions expected from Eqs. (28) and (31), valid for low and high  $P$ , and shown as a solid and dashed line respectively.

of Eq. (28). Apart from an over-prediction by a factor of about 5, there is good agreement between model and code for small, but not for large  $P$ , where Eq. (28) tends to overestimate. The dashed line is the prediction of Eq. (31) with  $R_{\min} = 1$  nm. The code results are in good agreement with this model for high values of  $P$ . These calculations demonstrate the cross-over between the two analytical results derived earlier. The agreement between

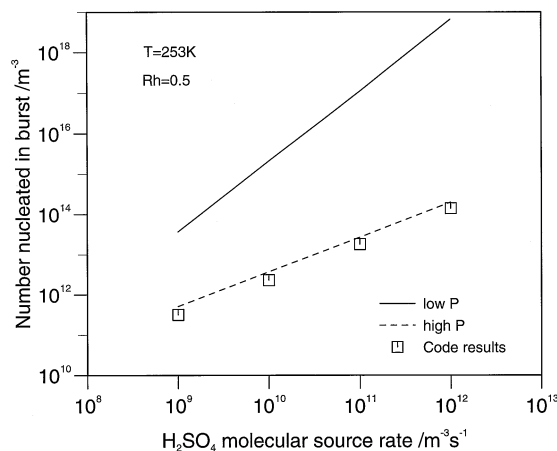


Fig. 3. Comparison of nucleated particle number densities according to Eq. (28) (solid line) and Eq. (31) with  $R_{\min} = 1$  nm (dashed line); and the numerical aerosol code (squares), at 253 K and  $R_h = 0.5$ , showing that the high production rate analytical result is a good fit for such conditions.

code calculations and analytical results is also tested at  $T = 253$  K and  $R_h = 0.5$  in Fig. 3. We compare the low  $P$  (circles) and high  $P$  (squares) analytic predictions with the code results (triangles). At this temperature, the cross-over is shifted to very much lower values of  $P$ , and all the code calculations are consistent with Eq. (31), with good accuracy if  $R_{\min}$  is set equal to 1 nm.

We are confident that Eqs. (28) and (31) can provide a reasonable estimate of the particle productivity of nucleation bursts for a wide variety of atmospheric conditions, as long as there is no initial aerosol present, and assuming the temperature is constant during the burst. We have not taken into account agglomeration which can reduce the number density, but this is properly a part of the subsequent aerosol dynamics.

#### 2.4. From sub-grid to grid scales

Although the burst models described here might provide reasonable descriptions of individual events in the atmosphere, further development has to be undertaken to make them suitable for use in global circulation models, which use a spatial scale of hundreds of km and timescales which are usually longer than the burst time-scale. The problem to be overcome is to assign a frequency for the conditions which lead to bursts. The effective nucleation rate which would appear in a coarse grid-scale model of aerosol evolution would be  $J_{\text{eff}} = N V_b \nu$  where  $\nu$  is the frequency of occurrence of bursts, per unit volume of atmosphere, and  $V_b$  is the volume which is affected by an individual burst.  $N$  should now be viewed as a burst productivity averaged over a distribution of

atmospheric conditions. The major difficulty in making progress is a lack of knowledge regarding the frequency  $\nu$ . However, it is likely that observational data will provide this missing ingredient. Possibly the most promising line of development will be to pursue the modelling to a point where experimental data for the present-day atmosphere will provide empirical fits to the unknown quantities, allowing predictions to be made regarding the effects of increased pollution in the future.

### 3. Barrierless nucleation

There is no free energy barrier to nucleation when all clusters, however small, are stable and do not decay. This perhaps represents the situation with ammonium sulphate molecules in the atmosphere. The theory described above for homogeneous nucleation can be used for this case, simply by using an appropriate nucleation rate, but we develop here an equivalent model which contains similar physics but which can be extended to illustrate competition with condensation on an existing aerosol. The main difference is that there are no decay terms in the cluster evolution equations. We focus on the evolution of the molecular concentration of sulphuric acid, and assume that there is always sufficient ammonia present to convert sulphuric acid to ammonium sulphate. To construct a rate theory for the three components  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4$  would be difficult and is outside the scope of this work.

#### 3.1. Population dynamics

Lushnikov and Kulmala (1995) have developed a theory for the nucleation and growth of stable clusters starting from monomers. We now extend this theory to include monomer removal onto existing aerosol, and a variable production rate. We calculate the time at which the removal of the ammonium sulphate monomer by the clusters previously formed becomes significant. Before this occurs, monomer removal will be dominated by deposition on the existing aerosol. The nucleation rate

is

$$J(t) = \alpha_1 c_1(t)^2, \quad (32)$$

where  $c_1$  is the monomer concentration, and  $\alpha_1$  is the collision probability for two monomers to meet and form a dimer. We assume that this is determined by the probability for a collision between two spheres of molecular volume  $v$  at a temperature  $T$

$$\alpha_1 = 16 (3v/4\pi)^{2/3} (\pi kT/M)^{1/2}, \quad (33)$$

where  $M$  is the molecular mass and  $k$  is Boltzmann's constant. For ammonium sulphate with a molecular weight of 132.14 g and a solid density of 1.77 g cm<sup>-3</sup>, this gives  $1/2\alpha_1 = 1.842 \times 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup>. The collision rate between a monomer and a cluster of  $n$  molecules is

$$\begin{aligned} \alpha_n &= 2(3v/4\pi)^{2/3} (1 + n^{1/3})^2 (2\pi kT/M)^{1/2} [(1+n)/n]^{1/2} \\ &\approx \alpha_g n^{2/3} = 2(3v/4\pi)^{2/3} (2\pi kT/M)^{1/2} n^{2/3} \end{aligned} \quad (34)$$

for large  $n$ , in which case  $\alpha_g = 6.514 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>.

The equation for the monomer concentration is

$$\begin{aligned} dc_1/dt &= P(t) - R_A c_1 - \alpha_1 c_1(t)^2 \\ &\quad - c_1(t) \sum_{n=2} \alpha_n c_n(t) \end{aligned} \quad (35)$$

where the  $n$ -cluster populations  $c_n(t)$  have been formed from time  $t = 0$  by the dimer nucleation term  $J(t)$ . The monomer production rate  $P(t)$  is that of sulphuric acid and is in the range  $10^4$ – $10^6$  cm<sup>-3</sup> s<sup>-1</sup>. As long as its value is not changing rapidly, the monomer concentration before growth on the nucleated aerosol is significant is then

$$c_1(0) = P(0)/R_A \quad (36)$$

The nucleation rate given by Eqs. (32) and (36) is shown in Table 1, for various values of  $P$  and  $R_A$ .

If  $R_A^2 \gg \alpha_1 P$ , the nucleation term in Eq. (35) is negligible in comparison with the aerosol removal term, and this is always satisfied for the removal timescales of interest. However, the final term from the growth of nucleated aerosol may become considerable and terminate the burst, as we saw happen in the model in Section 2. The sum is approximated by an integral and  $c_n(t)$  treated as

Table 1

Barrierless nucleation rates corresponding to aerosol removal timescales. The range of values correspond to a range in monomer production rate of  $P = 10^4$ – $10^6$  cm<sup>-3</sup> s<sup>-1</sup>

Removal time $t_A = R_A^{-1}$	Molecular concentration $c_1$ (cm <sup>-3</sup> )	Nucleation rate $J$ (cm <sup>-3</sup> s <sup>-1</sup> )
1 s	$10^4$ – $10^6$	0.018–184
15 s	$1.5 \times (10^5$ – $10^7)$	$4.15$ – $4.15 \times 10^4$
1 min	$6 \times (10^5$ – $10^7)$	$66.3$ – $6.63 \times 10^5$
10 min	$6 \times (10^6$ – $10^8)$	$6.63 \times 10^3$ – $6.63 \times 10^7$
1 h	$3.6 \times (10^7$ – $10^9)$	$2.4 \times 10^5$ – $2.4 \times 10^9$

a continuous function  $c(n, t)$ . The trajectories of  $n$  arising from  $n = 2$  at time  $t'$ , to  $n$  at time  $t$  are solutions of

$$dn/dt = \alpha(n)c_1(t), \tag{37}$$

where  $\alpha(n)$  is a continuous representation of  $\alpha_n$ . We obtain

$$(3/\alpha_g)(n^{1/3} - 2^{1/3}) = \int_{t'}^t c_1(t_1) dt_1 \approx c_1(0)(t - t'). \tag{38}$$

The particle source term at time  $t'$  is

$$J(t') = 1/2\alpha_1 c_1^2(t') \approx 1/2\alpha_1 c_1^2(0) \tag{39}$$

and we again use the form

$$c(n, t) = - [\partial t'(n, t)/\partial n]J(t'). \tag{40}$$

The removal rate onto the freshly nucleated aerosol in Eq. (35) is then

$$\begin{aligned} R_N &= c_1(t) \int_2^n dn' \alpha(n') c(n', t) \\ &= c_1(t) \int_0^t dt' \alpha(n(t, t')) \alpha_1 c_1^2(0) \end{aligned} \tag{41}$$

where we have substituted from Eqs. (39) and (40) and changed the integration variable. The dependence of  $n$  on time is obtained from Eq. (38), omitting the  $2^{1/3}$  in comparison with  $n^{1/3}$ , and we obtain:

$$\begin{aligned} R_N &= 1/2\alpha_1 (\alpha_g^3/27) c_1^4(0) c_1(t) t^3 \\ &\approx 1/2\alpha_1 (\alpha_g^3/27) c_1^5(0) t^3. \end{aligned} \tag{42}$$

The rate of vapour removal by particle nucleation rises rapidly with time.

### 3.2. Competition with condensation on an existing aerosol

Assuming the monomer concentration is determined by removal onto existing aerosol, we can use Eqs. (36) and (42) to estimate the timescale  $t_c$  for the removal rate onto the nucleated aerosol  $R_N$  to become equal to the production rate  $P$ :

$$t_c = 8.09 \times 10^{13} / (P^{4/3} t_A^{5/3}) s \tag{43}$$

where we have used the values of  $\alpha_g$  and  $\alpha_1$  given above, and  $P$  is in  $\text{cm}^{-3} \text{s}^{-1}$  and  $t_A$  in s. In Table 2 we give values of  $t_c$  corresponding to the removal timescales used in Table 1. The results clearly show the sensitivity of barrierless nucleation to the amount of aerosol already present ( $t_A$  or  $R_A$ ) and to the monomer production rate  $P$ . If the calculated timescales  $t_c$  are long, it means that nuclea-

Table 2

Timescales  $t_c$  for condensation on particles nucleated by barrierless nucleation to affect the monomer concentration for different aerosol removal timescales  $t_A$ . The monomer production rate is  $P = 10^4 - 10^6 \text{ cm}^{-3} \text{ s}^{-1}$

Removal time $t_A = R_A^{-1}$	Production rate		
	$P = 10^4$	$P = 10^5$ ( $\text{cm}^{-3} \text{ s}^{-1}$ )	$P = 10^6$
1 s	12 yr	6 months	9.4 h
15 s	48 days	2.2 days	2.5 h
1 min	4.7 days	5.3 h	15 min
10 min	2.4 h	6.8 min	19 s
1 h	7.4 min	21 s	1 s

tion is unlikely to control the dynamics:  $P$  or  $R_A$  are likely to change more rapidly. The nucleation rate will proceed at the rates given in Table 1, and the nucleation and growth processes could be incorporated into a equation for  $c_1(t)$  solved numerically on the long timescales of global atmospheric models. However, if  $t_c$  is less than  $t_A$ , which occurs towards the bottom right hand corner of Table 2, then the dynamics produce a nucleation pulse, cut off by condensation on the nucleation mode as considered in Section 2.2. Bursts of barrierless nucleation must then be described in a sub-grid fashion, using simplified models. A similar approach is used in Appendix B to determine the removal timescales for the homogeneous nucleation mechanism.

### 3.3. Dependence on molecular sticking probability

In all the work hitherto we have assumed that growth takes place with molecular sticking probabilities equal to unity. However,  $S_p = 0.02$  has been used for sulphuric acid molecules (Van Dingenen and Raes, 1991). The change in our results will depend on whether growth on the existing larger size aerosol is in the molecular ( $R_A \propto S_p$ ) or continuum ( $R_A$  independent of  $S_p$ ) regimes, in which cases either  $c_1(0)$  is approximately proportional to  $1/S_p$ , or is independent of  $S_p$ , respectively. The factor  $\alpha_g$  in Eq. (34) is proportional to  $S_p$ . We have

$$\begin{aligned} t_c^3 &\propto (P^4 \alpha_1 \alpha_g^3 c_1^5(0))^{-1} \propto S_p^2, \quad \text{for } R_A \propto S_p \tag{44} \\ &\propto S_p^{-3}, \end{aligned}$$

$$\text{for } R_A \text{ independent of } S_p. \tag{45}$$

For most of the aerosols considered by Clement and Ford (1997),  $R_A \propto S_p$ , so that timescales  $t_c$  will be reduced by a factor  $S_p^{2/3} = 0.074$  when  $S_p$  is reduced from 1 to 0.02. We would also expect an increase in  $t_A$  as a result of this change.



#### 4. Conclusions

In this paper we have considered bursts of nucleation, which are believed to be the main atmospheric sources of particles derived from gas phase precursors. Bursts take place in special circumstances, particularly where the atmosphere is locally free of aerosol which might provide a stronger sink for vapour condensation. Local cleansing of the atmosphere, due to a precipitation event, for example, might be followed by a nucleation burst. We have developed analytical models to calculate the number of particles nucleated in such a burst.

We have discussed two particle formation mechanisms: the binary homogeneous nucleation of sulphuric acid/water droplets; and the reaction of ammonia with sulphuric acid to produce ammonium sulphate, which leads to particle nucleation by so-called barrierless nucleation. This is likely to be the main formation mechanism for particles close to urban and rural sources of ammonia: elsewhere binary sulphuric acid/water condensation is likely to dominate.

Bursts are modelled by solving the dynamical equation for the time-dependent gas phase concentration of the condensable material. We have considered in particular bursts during which the freshly nucleated mode provides the major sink for vapour. We have studied various approximations which simplify the solution of the equation, particularly one where the vapour concentration is modelled as a parabolic function of time about its peak, and another where the nucleation rate is modelled as a Gaussian in time. For a given nucleation rate, growth rate and production rate for condensable vapour, it is possible to obtain analytical forms for the number of particles formed during a burst. Two expressions have been obtained for high and low vapour production rates. The accuracy of these expressions has been checked using a detailed aerosol dynamics code.

We have also extended the model of Lushnikov and Kulmala (1995) for barrierless nucleation, to provide an alternative approach to the burst dynamics for this mechanism. We have calculated the vapour depletion rate due to nucleation for this model and compared the timescale for this with timescales for condensation on an existing aerosol, to reveal when competitive condensation onto such an aerosol plays a role.

The simple models we have proposed are suitable for determining the number of particles produced by a single burst for particular atmospheric conditions. There is much to do in comparing model predictions with observational experience, particular with regard to spatial fluctuations. There is also much to be done in developing simplified dynamics of the full dynamics of the atmospheric aerosol, to find how sensitive the average aerosol parameters are to the single burst particle production rate, and ultimately to the vapour source term. The achievement of these goals should reveal how the atmo-

spheric aerosol, and the climate, are likely to change as a result of human activities.

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#### Appendix A. Gaussian approximation for barrierless nucleation bursts

The Gaussian form, Eq. (20), for the nucleation rate may appear to be unrealistic when calculating the number of nuclei produced by a burst when  $\beta = 2$  and the nucleation rate is given by

$$J(t) = \alpha_1 \rho(t)^2. \quad (\text{A.1})$$

Accordingly, we introduce an alternative model in which we integrate over the nucleation peak using this exact form for  $J$ , but where  $\rho$  still takes the approximate form in Eq. (19). To simplify the integration, the initial time  $t_i$  is taken to correspond to  $\rho = 0$ , and thus

$$t_m - t_i = [-2 \rho_m / \rho_m'']^{1/2}. \quad (\text{A.2})$$

We now introduce the variable  $u = \rho_m - \rho$  so that

$$\begin{aligned} d\rho/dt &= -du/dt = [-2\rho_m''(\rho_m - \rho)]^{1/2} \\ &= [-2\rho_m''u]^{1/2}. \end{aligned} \quad (\text{A.3})$$

The total number produced by a burst is

$$\begin{aligned} N &= 2 \int_{t_i}^{t_m} J(\rho(t')) dt' \\ &= 2 \int_0^{\rho_m} 1/2 \alpha_1 (\rho_m - u)^2 / [-2\rho_m''u]^{1/2} du \\ &= (22/15) \alpha_1 \rho_m^{5/2} / [-2\rho_m'']^{1/2}. \end{aligned} \quad (\text{A.4})$$

We also have

$$P(t_m) = 4\pi \mu_a \rho_d \rho_m \int_0^{t_m} J(\rho(t')) R^2(t_m, t') dt' \quad (\text{A.5})$$

where

$$R(t_m, t') = \eta \mu [\rho_m(t_m - t') + \rho_m''(t_m - t')^3/6]. \quad (\text{A.6})$$

In barrierless nucleation it should always be possible to neglect the initial value of  $R$ . Keeping the second term in Eq. (A.6), we evaluate the integral in Eq. (A.5) by

Table A1  
Numerical coefficients for different evaluations of nucleation bursts for barrierless nucleation

Quantity	Coefficient	Eq.	Gaussian $J^a$	Exact $J$
$N$	$A$	A4	$\pi^{1/2} = 1.722$	$22/15 = 1.467$
$P$	$B$	A7	$\pi^{3/2} = 5.568$	$15104\pi^{1/2}/31185 = 2.152$
$\rho_m''$	$C$	A8	$4\pi = 12.57$	$11\pi/9 = 3.84$

<sup>a</sup>In this evaluation, the  $t^3$  term for  $R$  in Eq. (A.6) is neglected.

changing the variable to  $u$  to obtain

$$P = (15104\pi^{1/2}/31185) \times [1/2\alpha_1\rho_d\eta^2\mu^3\rho_m^{13/2}/(-2\rho_m'')^3]^{1/2}. \quad (\text{A.7})$$

Similarly we have

$$\rho_m'' = -4\pi\mu\rho_d\rho_m \int_0^{t_m} J(\rho(t'))2R(t_m, t') \times \partial R(t = t_m, t')/\partial t dt' \quad (\text{A.8})$$

and the derivative is just  $\eta\mu\rho_m$ . Then

$$\rho_m'' = -(11\pi/9)[\alpha_1\rho_d\eta^2\mu^3\rho_m^6/(-\rho_m'')]. \quad (\text{A.9})$$

The three results for  $N$ ,  $P$  and  $\rho_m''$  have the same dependence on their variables as the  $\beta = 2$  case of the general results (22), (24) and (25) obtained using the Gaussian form for  $J$ . The differences in the numerical coefficients are summarised in Table A1. These differences have only a small effect, for example

$$N = [AC^{1/8}/(2B)^{1/2}]P^{1/2}/(1/2\alpha_1\rho_d\eta^2\mu^3)^{3/8}. \quad (\text{A.10})$$

The numerical coefficient in square brackets changes from 0.6953 in the Gaussian case to 0.8366 in the exact case, an increase of only 20%. This small change gives us some confidence that the Gaussian results can be applied across the whole range of possible  $\beta$  with only slight loss of accuracy.

## Appendix B. Homogeneous nucleation removal rate

The analysis presented in Section 3 for barrierless nucleation can be adapted to determine the time  $t_c$  for a homogeneous nucleation process to affect the vapour concentration. In Section 2 we found that nucleation is cut off in a time  $t_m$ , given in Eq. (27). We now obtain an alternative estimate, which also takes into account competitive condensation on an existing aerosol.

The theory for barrierless nucleation can be applied with  $J = J_0S^\beta$  (Easter and Peters, 1994). Using Eq. (42), the removal rate is  $J_0(\alpha^3/27)c_1(0)^3S^\beta t^3$ . By putting this equal to  $P$  and writing

$$S = S_0(T)c_1(0) = S_0(T)Pt_A \quad (\text{B.1})$$

Table B1

Timescales  $t_c$  for condensation on particles nucleated by homogeneous nucleation (at Rh = 1 and  $T = 0^\circ\text{C}$ ) to affect the monomer concentration for different aerosol removal timescales  $t_A$ . The monomer production rate is  $P = 10^4$ – $10^6 \text{ cm}^{-3} \text{ s}^{-1}$

Removal time $t_A = R_A^{-1}$	Production rate		
	$P = 10^4$	$P = 10^5$ ( $\text{cm}^{-3} \text{ s}^{-1}$ )	$P = 10^6$
1 s	—	—	> 1000 yr
15 s	—	120 yr	19.7 days
1 min	> 1000 yr	266 days	2.9 hr
10 min	123 days	80 min	2.16 s
1 h	4.05 h	6.57 s	0.003 s

we can find the timescale  $t_c$  for the monomer concentration to be affected by the nucleation process. This procedure is similar to that followed by Shaw (1989). We get

$$t_c = 4.605 \times 10^{10} / [J_0^{1/3} S_0(T)^{\beta/3} P^{(\beta+2)/3} t_A^{\beta/3+1}]. \quad (\text{B.2})$$

Time scales calculated using the above formula for  $T = 0^\circ\text{C}$  and Rh = 1 when  $J_0 = 1.45 \times 10^{26} \text{ cm}^{-3} \text{ s}^{-1}$  and  $\beta = 8.04$  (Easter and Peters, 1994) are shown in Table B1. Cleaner initial conditions correspond to rows further down the table. For short timescales  $t_A$  and low values of  $P$  there is no significant homogeneous nucleation: it takes extremely long times for nucleation to affect the dynamics, and other terms in Eq. (1) dominate the evolution. However, as  $t_A$  and  $P$  increase, the cut-off time decreases drastically, and eventually condensation on the nucleated aerosol will control the timescale of the burst. The sensitivity to the presence of an initial aerosol, represented as a removal timescale  $t_A$ , is illustrated in the Table. Simplified burst models are useful when  $t_c$  is less than  $t_A$  and of order minutes or less.

## Appendix C. Source limited nucleation bursts

When insufficient nuclei are produced for their growth to cut off nucleation, the molecular source rate  $P(t)$

controls the burst. We consider a time period from  $t = 0$  to  $\pi/\omega$ , during which the rate varies sinusoidally:

$$P(t) = P \sin \omega t. \quad (\text{C.1})$$

Vapour loss to the nucleation mode is now neglected compared to loss to existing aerosol, so that Eq. (12) for the molecular concentration reduces to

$$d\rho/dt = P \sin \omega t - \rho R_A. \quad (\text{C.2})$$

For simplicity we assume  $R_A$  is time independent. The solution is then

$$\begin{aligned} \rho = & \rho_0 \exp(-R_A t) + (P/R_A) \\ & \times [\sin \omega t - (\omega/R_A)(\cos \omega t - \exp(-R_A t))] \\ & / (1 + \omega^2/R_A^2). \end{aligned} \quad (\text{C.3})$$

The initial value  $\rho_0$  will be neglected. The maximum occurs when  $d\rho/dt = 0$  or

$$\cos \omega t + \omega/R_A \sin \omega t - \exp(-R_A t) = 0. \quad (\text{C.4})$$

The peak occurs at  $t = t_m$  between  $t = \pi/2\omega$  and  $t = \pi/\omega$ . Typical values for  $R_A$  for atmospheric aerosols correspond to timescales of the order of minutes at most. For situations favouring nucleation they may be somewhat longer, but as long as timescales for the variation of  $P(t)$  (i.e.  $\omega^{-1}$ ) are not much shorter, and this is generally unlikely in the atmosphere, we can ignore the final term in Eq. (C.4) since it is smaller than  $\exp(-\pi R_A/2\omega)$ . The equation can then be solved for  $t_m$ :

$$t_m = (1/\omega) (\pi/2 + \tan^{-1}(\omega/R_A)). \quad (\text{C.5})$$

Again neglecting the exponential terms in Eq. (C.3), the value of  $\rho$  and its second derivative at the peak are given by

$$\rho_m = P/(R_A^2 + \omega^2)^{1/2} \quad (\text{C.6})$$

and

$$\rho_m'' = -\omega^2 \rho_m. \quad (\text{C.7})$$

The total number of particles nucleated during this vapour density pulse is then obtained from Eq. (25):

$$N = (2\pi/\beta)^{1/2} J(P/(R_A^2 + \omega^2)^{1/2}) (1/\omega). \quad (\text{C.8})$$

This expression can be compared to values obtained by using the exact value of  $\rho$  from Eq. (C.3) and the original nucleation rate given by Eq. (18). Note that it

contains a strong sensitivity to  $P$ , in contrast to the expressions (28) and (31).

## References

- Ayers, G.P., Gillett, R.W., Gras, J.L., 1980. On the vapor pressure of sulfuric acid. *Atmospheric Environment* 15, 1221–1225.
- Barrett, J.C., 1992. Nucleation with changing supersaturation. *Journal of Aerosol Science* 23, S141–144.
- Barrett, J.C., Clement, C.F., 1991. Aerosol concentrations from a burst of nucleation. *Journal of Aerosol Science* 22, 327–335.
- Clement, C.F., 1978. Solutions of the continuity equation. *Proceedings of the Royal Society of London A* 364, 107–119.
- Clement C.F., Ford, I.J., 1998. Gas-to-particle conversion in the atmosphere: I. Evidence from empirical atmospheric aerosols. *Atmospheric Environment* 33, 475–487.
- Clement, C.F., Kulmala, M., Vesala, T., 1996. Theoretical consideration on sticking probabilities. *Journal of Aerosol Science* 27, 869–882.
- Easter, R.C., Peters, L.K., 1994. Binary homogeneous nucleation: temperature and relative humidity fluctuations, nonlinearity, and aspects of new particle production in the atmosphere. *Journal of Applied Meteorology* 33, 775–784.
- Ford, I.J., Clement, C.F., 1998. Work in progress.
- Friedlander, S.K., 1978. A note on new particle formation in the presence of an aerosol. *Journal of Colloid and Interface Science* 67, 387–388.
- Jones, A., Roberts, D.L., Slingo, A., 1994. A climate model study of indirect radiative forcing by anthropogenic sulphate aerosols. *Nature* 370, 450–453.
- Lushnikov, A.A., Kulmala, M., 1995. Source-enhanced condensation in monocomponent systems. *Physical Review E* 52, 1658–1668.
- McGraw, R., Saunders, J.H., 1984. A condensation feedback mechanism for oscillatory nucleation and growth. *Aerosol Science and Technology* 3, 367–380.
- Pratsinis, S.E., 1988. Simultaneous nucleation, condensation and coagulation in aerosol reactors. *Journal of Colloid and Interface Science* 124, 416–427.
- Shaw, G.E., 1989. Production of condensation nuclei in clean air by nucleation of  $\text{H}_2\text{SO}_4$ . *Atmospheric Environment* 23, 2841–2846.
- Weber, R.J., Marti, J.J., McMurry, P.H., Eisele, F.L., Tanner, D.J., Jefferson, A., 1996. Measured atmospheric new particle formation rates: implications for nucleation theory. *Chemical Engineering Communications* 151, 53–64.
- Van Dingenen, R., Raes, F., 1991. Determination of the condensation accommodation coefficient of sulfuric acid on water-sulfuric acid aerosol. *Aerosol Science and Technology* 15, 93–106.