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Time lag effects on the binary homogeneous nucleation of aerosols in the wake of an aircraft

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Abstract. Steady state rates and time lags for binary homogeneous nucleation of sulfuric acid-water aerosols in aircraft wakes are calculated for relative humidities lower than 100%, i.e., for the case in which no visible contrails form. Formation of the sulfuric acid-water aerosol is shown to depend sensitively on the concentration of sulfuric acid derived from engine exhaust. Nucleation of the sulfuric acid-water aerosol is found to be controlled both by the steady state rate and by the time lag on the timescales relevant to contrail formation. Only for the highest gas-phase acid concentrations are the nucleation time lags sufficiently short that steady state conditions pertain.

Introduction

Civil aviation releases various components that can affect natural atmospheric processes. Perturbations of tropospheric chemistry by these effluents may contribute to anthropogenically induced climate change if they are large enough to modify the Earth's radiative budget balance, either directly by increasing "greenhouse" gases or indirectly by altering cloud formation processes at flight altitudes.

Emissions of water vapor, sulfur dioxide, and soot particles by jet engines may induce the formation of new particles, i.e., aerosols and contrails. Depending upon the climatic conditions, long-lived ice clouds may be formed by direct condensation of water vapor on preexisting particles (mostly soot released by the engines); these ice clouds may enhance the greenhouse effect because of their high emissivity and low albedo in the IR and VIS, respectively.

In addition, the sulfur released by the engines may be converted to aerosols by simultaneous nucleation of sulfuric acid and water vapors (hereafter referred to as binary nucleation). The amount of aerosol formed with this process is unlikely to perturb the radiative balance of the atmosphere through direct forcing. However, it is generally believed that these newly formed particles may act as nucleation centers for contrail formation and may also act later as cloud condensation nuclei (CCN). Any increase in the number concentration of these CCN has the potential for increasing the occurrence and optical thickness of clouds. Specifically, because the altitude of formation of cirrus clouds coincides with the altitude of subsonic aircraft flights, an indirect effect of aerosol formation is to increase the CCN concentrations (and possibly ice nuclei concentrations) at these elevations, possibly resulting in an increased concentration of cloud droplets and ice crystals.

Several recent theoretical studies [*Miake-Lye et al.*, 1994; *Taleb and Mirabel*, 1995; *Brown et al.*, 1996] suggest that binary nucleation of H_2SO_4 (formed from the oxidation of SO_2) and water vapors occurs first in the wakes, followed eventually (depending upon local meteorological conditions) by heterogeneous condensation of water either on these new particles or on soot particles (or on their agglomerates [*Kärcher et al.*, 1995]). These predictions, based on the classical steady state theory of homogeneous binary nucleation (including or not including hydrate formation), lead to the formation of an extremely high concentration of aerosols in the wake, namely, 10^8-10^{11} cm^{-3} at an axial distance of about 1000 m behind the engines.

The possible formation of theses acidic aerosols, first suggested by *Hofmann and Rosen* [1978], has been supported by several measurements [*Pitchford et al.*, 1991; *Frenzel and Arnold*, 1994; *Fahey et al.*, 1995]. More recently, the possible influence of sulfur emission (and resulting aerosol nucleation) on contrail formation was investigated by *Busen and Schumann* [1995]. For this study they used a jet aircraft in which two engines were burning fuels with different sulfur content (sulfur mass fraction 2 and 250 parts per million (ppm)) during the same flight. On the basis of the above theoretical calculations one would expect that if the acidic aerosols form first in the wake, visible differences will be observed between the two contrails (due to different particle number densities, start point of contrail formation, and other factors), which was not the case. However, in a later experiment in which the sulfur content for one engine was as high as 5500 ppm [*Schumann et al.*, 1996], i.e., well above the standard specifications, noticeable visual differences were observed between the two contrails, caused by the different sulfur levels. Hence the question of the impact of sulfur on contrail formation has not been fully resolved.

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However, a possible explanation of the observations of *Busen and Schumann* [1995] or *Schumann et al.* [1996] relies on the fact that the theoretical predictions are based on the steady state nucleation theory to calculate rates. This hypothesis may be invalid if the time needed to reach the steady state (time lag) is comparable to or longer than the experimental timescale.

The objective of this study is to present some theoretical developments on the influence of time lag on nucleation processes in a wake. It will be shown that aerosol nucleation rates are greatly influenced by the delay due to the time lag. Calculations ignoring this delay may be in error by several orders of magnitude.

Method

All the developments presented here, as well as the previous works cited in the introduction, have been performed in the frame of the "classical" theory of binary nucleation. Although subject to many shortcomings, this phenomenological approach is very attractive because it utilizes macroscopic measurables such as surface tension and chemical potentials in its prediction of the nucleation rate. The classical binary theory was originated by *Volmer* [1939] and given a more complete theoretical treatment by *Reiss* [1950]. The theory was applied to the sulfuric acid-water mixtures by *Doyle* [1961], *Kiang and Stauffer* [1973], and *Mirabel and Katz* [1974] and later improved by *Heist and Reiss* [1974], *Shugard and Reiss* [1976], *Jaecker-Voirol et al.* [1987], and *Jaecker-Voirol and Mirabel* [1988], who took into account hydrate formation in the vapor phase. These and many subsequent works confirm that exceedingly small amounts of sulfuric acid in the vapor phase are able to induce the nucleation of water. However, as we mentioned in the introduction, these predictions rely implicitly on the existence of steady state nucleation conditions. If the steady state assumption is valid when the time to reach the steady state is short in comparison with the timescale of the experiment, it fails when the time lag becomes large, which may be the situation for the formation of H_2SO_4-H_2O aerosols in aircraft wakes. In this case, transient behavior must be considered, as was done, for example, by *Schelling and Reiss* [1981b] in their studies of this mixture. These authors found that under some specific conditions, predictions of the time lags in the H_2SO_4-H_2O system can be as long as seconds, if not tens of seconds, in contrast to the much shorter timescale (microseconds) obtained for the nucleation of water alone.

In the following treatment, some specific simplifications, applicable to the H_2SO_4-H_2O mixture, will be made. First, because of the very high dissymmetry between the vapor pressures of water and sulfuric acid (about 10 orders of magnitude) found in the atmosphere it is assumed that, between the incorporation of sulfuric acid molecules in a cluster, a cluster is in quasi equilibrium with respect to exchange of water molecules [*Mirabel and Katz*, 1974]. Second, we will assume that most of the acid molecules in the gas phase are hydrated; a hydrate being composed of *1* acid and *h* water molecules. Hydrates containing higher numbers of acid molecules are not considered here, since it has been shown previously that the *1,h* hydrates dominate the others by several order of magnitude [*Jaecker-Voirol and Mirabel*, 1988].

Matrix Formulation for Relaxation Time Distribution

According to the above simplifications, the general differential equation expressing the time dependence of the number density f_{ij} of a cluster containing i water and j acid molecules is [*Reiss*, 1950; *Schelling and Reiss*, 1981a; *McGraw*, 1995]

$$\frac{df_{ij}}{dt} = I_{i-1,j} + J_{i,j-1} - I_{i,j} - J_{i,j} \tag{1}$$

where I and J refer to the net currents due to addition of water and acid molecules per unit volume, respectively. Assuming that the quasi equilibrium of water is established, the net currents I are zero. Thus the time dependence of the number densities can be written as

$$\frac{df_{ij}}{dt} = J_{i,j-1} - J_{i,j} \tag{2}$$

The net rate of acid addition is

$$J_{i,j} = \nu_{i,j} f_{i,j} - \gamma_{i,j+1} f_{i,j+1} \tag{3}$$

where $\gamma_{i,j+1}$ refers to the evaporation rate for loss of an acid from an $i,j+1$ cluster and $\nu_{i,j}$ is the collision rate between a cluster of size i,j and hydrates. Following *Shugard et al.* [1974], $\nu_{i,j}$ is given by an average over hydrate species:

$$\nu_{i,j} = (8\pi kT)^{1/2} \sum_h \sigma_h^2 \mu_h^{-1/2} N_{h,1} \tag{4}$$

where σ_h is the sum of the radii of the colliding species, μ_h is the corresponding reduced mass, k is the Boltzmann constant, and T is the temperature. $N_{h,1}$ is the equilibrium number density of $1,h$ hydrates [*Jaecker-Voirol and Mirabel*, 1988]. If the formation of hydrates is ignored, as it was done in many previous studies, equation (4) reduces to the collision frequency between the acid molecules and the i,j clusters. Note, in connection with equations (2) and (3), that the addition and loss of hydrate species will also change the water index (i). However, since water collisions dominate, any contribution to changes in water index from hydrate exchange will be insignificant in comparison with the fluxes due to exchange with water vapor itself. Consequently, we can neglect changes in the water index due to hydrate exchange [*McGraw*, 1995].

Evaporation rates, $\gamma_{i,j+1}$, can be derived by using the equilibrium (J_{ij}=0) detailed balance condition

$$\gamma_{i,j+1} = \nu_{i,j} \frac{N_{i,j}}{N_{i,j+1}} \tag{5}$$

where N_{ij} , the equilibrium number densities of clusters i,j, is given by

$$N_{ij} = N_t \exp(-\Delta G(i,j)/kT). \tag{6}$$

N_t is the total number of molecular species in the vapor phase. Since the number density of water molecules $N_{1,0}$ far exceeds that of acid molecules and of hydrates, $N_t \approx N_{1,0}$. $\Delta G(i,j)$ represents the free energy of formation of i,j clusters, including hydrates [see *Jaecker-Voirol and Mirabel*, 1988]. Elimination of the evaporation rates using equation (6) and summation over the water index (i) yields [*Schelling and Reiss*, 1981a]

$$\frac{df_j}{dt} = \left(\frac{\nu_{j-1}N_{j-1}}{N_{j-1}}\right) f_{j-1} - \left(\frac{\nu_{j-1}N_{j-1}}{N_j} + \frac{\nu_j N_j}{N_j}\right) f_j + \left(\frac{\nu_j N_j}{N_{j+1}}\right) f_{j+1} \tag{7}$$

where the following quantities have been defined:

$$f_j = \sum_i f_{i,j}\,,\quad N_j = \sum_i N_{i,j} \quad \nu_j N_j = \sum_i \nu_{i,j} N_{i,j}$$

This equation can be expressed in a matrix-vector form (equation (8)), if we consider the usual Szilard boundary condition, i.e., $f_1 = N1$ and $f_j/N_j = 0$, for large enough values of j.

$$\frac{df}{dt} = Kf + a \tag{8}$$

Here, $f = (f_1, f_2, \ldots, f_{jmax})^T$ is the population vector ($jmax$ is the maximum number of acid molecules considered per cluster), and $a = (\nu_{1,0}N_{1,0}, 0, 0, \ldots, 0)$ is a constant vector dependent on the water vapor concentration. The tridiagonal matrix K contains the coefficients appearing on the right-hand side of equation (9):

$$K_{j,j-1} = \frac{\nu_{j-1} N_{j-1}}{N_{j-1}}, \qquad K_{j,j+1} = \frac{\nu_j N_j}{N_{j+1}}$$

$$K_{j,j} = -\left[\frac{\nu_{j-1} N_{j-1}}{N_j} + \frac{\nu_j N_j}{N_j}\right] \tag{9}$$

Time-dependent nucleation properties follow from the eigenvalues and eigenvectors of a Hermitian matrix H obtained through similarity transformation of K by a diagonal matrix:

$$H = -D^{1/2} \bullet K \bullet D^{-1/2} \tag{10}$$

Elements of D are the Boltzmann factors (summed over i) in terms of which equilibrium number densities are defined ($D_{j,j} = N_j/N_t$). Since the transformation matrices are diagonal, the H matrix has the tridiagonal band structure of K but is also in symmetric form. Eigenvalues of H determine the inverse relaxation times for the nonsteady nucleation process. The time lag, defined as the inverse of the smallest eigenvalue, provides a useful measure of the time required to reach the steady state.

Note that in order to establish the nucleation timescale we assume that the environmental conditions are constant over the time interval necessary to achieve a steady state nucleation rate. Specifically, the temperature, sulfuric acid concentration, and water vapor concentration are treated as constants in the analysis of equations (7)-(10). Thus the matrix elements of K and the elements of the vector a in equation (8), which are derived from these quantities, are constant. Elements of the population vector f change with time, while the equilibrium number densities, determined by the environmental conditions through the Boltzmann distribution (equation (6)), are fixed. Once the nucleation timescale has been obtained from the eigenvalues of H, as described above, it can be compared with the timescale over which significant changes in the environmental variables take place in the wake. This comparison, carried out in the following section, provides a rigorous basis for testing the validity of assuming a steady state nucleation rate.

The homogeneous nucleation rate at steady state J_{ss} is calculated numerically [*Shugard et al.*, 1974] as

$$J_{ss} = \left(\sum_j \frac{1}{\nu_j N_j}\right)^{-1} \tag{11}$$

Equation (11) also results as the steady state solution to equation (8), which can be derived by setting the left-hand side of equation (8) equal to zero.

During the transition period of approach to steady state a convenient closed form approximation to the nucleation rate can be used [*Shi and Seinfeld*, 1990; *Wyslouzil and Wilemski*, 1996]:

$$J_t = J_{ss} \exp\left(-\exp\left(2\left(\lambda - \frac{t}{\tau}\right)\right)\right) \tag{12}$$

where $\lambda = 0.5 \ln(\Delta G^*(i,j)/3kT)$, $\Delta G^*(i,j)$ is the formation free energy barrier at the critical point and τ is the time lag.

Construction of the D, K, and H matrices requires knowledge of a number of physical parameters as functions of temperature and concentration. Among the most crucial data are the differences of chemical potential between the liquid and gaseous phase for both constituents, the surface tension, the molar volume of the solution, and the hydration constant of H_2SO_4 in the gas phase. All these data have been taken from our previous work [*Jaecker-Voirol et al.*, 1987; *Jaecker-Voirol and Mirabel*, 1988, 1989], except for the chemical potential of the liquid sulfuric acid-water solution, which is now taken from a new compilation by *Taleb et al.* [1996].

We consider clusters containing from 0 to 6 acid molecules ($jmax$ = 6). This quantity corresponds to a reduced K matrix dimension, also of 6, for use in equation (8). This is a sufficient number of acids, as several articles have shown that under the atmospheric conditions used here the critical clusters contain only 1 or 2 sulfuric acid molecules [*Laaksonen and Kulmala*, 1991; *Kärcher et al.*, 1995]. Our present findings for the size of the critical nucleus also support these results. In summing over the water index (i), required for evaluation of the matrix elements appearing in equations (7) and (9), we included all clusters containing up to 100 water molecules ($imax$ = 100) in size. Eigenvalues of the symmetric tridiagonal H matrix were determined by using a computer subroutine from the LAPACK mathematical library. The inverse of the smallest eigenvalue corresponds to the relaxation time τ needed to reach a steady state nucleation rate.

Results and Discussion

The above theory will now be used to determine the time lag needed to achieve steady state nucleation rates for the typical case of a subsonic aircraft flying near the tropopause. Specifically, we consider a Boeing 767 equipped with two RB211 engines and flying at midlatitude, as this case has been subject to an extensive study under the AERONOX European programme [*Schumann*, 1995]. The flight conditions at an altitude of about 10 km are 240 mbar total pressure, 220 K ambient temperature, 28% relative humidity, and an emission index for H_2O of 1281 g/kg of fuel. Dynamical processes during the two first phases of the wake (the jet and the jet/vortex interaction) as studied in the AERONOX project result in the temperature and saturation ratio profiles depicted in Figure 1. Note that, under the chosen conditions, the saturation ratio relative to water barely reaches a maximum of 1 (i.e., relative humidity of 100%) after 0.8-0.9 s and as a consequence, no formation of visible contrail is expected.

The time lag as well as the steady state nucleation rate in the binary system H_2SO_4-H_2O is found below to depend very strongly upon the concentration of acid molecules available in the wake. Sulfuric acid is produced by the homogeneous gas-phase oxidation of the SO_2 released by engine fuel burning. Oxidation of SO_2 is driven by the reaction with OH radicals and occurs in the jet regime, i.e., in the first 0.1 s (first 30 m). This short reaction time is due to the rapid consumption of OH radicals by reactions with NO_x, leading to HNO_3, HNO_2, and N_2O_5. As a consequence, only a small fraction of SO_2 is converted into gaseous sulfuric acid. Typical conversion factors, deduced from modeling studies, range from about 2% [*Garnier*, 1995] to 0.6%

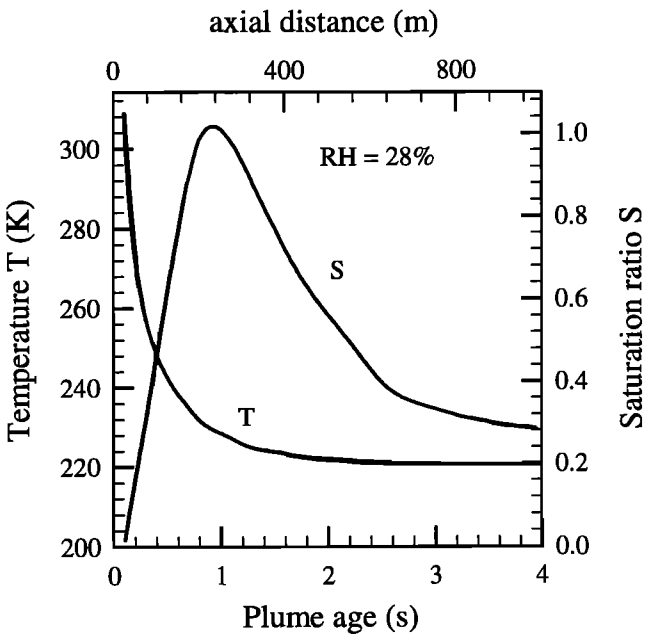

Figure 1. Evolution of the temperature T and of the water saturation ratio S as a function of plume age (or the axial distance), in the wake of a B767 jet engine.

[*Miake-Lye et al.*, 1994; *Brown et al.*, 1996] or 0.5% [*Kärcher et al.*, 1995]. However, recent in-flight measurements of volatile aerosols for Concorde wake indicate much higher conversion factors of 12% to 45% [*Fahey et al.*, 1995].

In addition to the sulfur content of the fuel and conversion rate of SO_2, acid concentrations are also strongly affected by the local flow dynamics, which control the dilution factor and the temperature. The production of particles seems to occur during the first second of the mixing between the jet and the vortex, a region of the wake that appears very difficult to model. For example, the dilution factor after 200 m as calculated by *Miake-Lye et al.* [1994] for a B707, or by *Woods and Hills* [1995] for a B767, is about 0.01, a value far below the estimate of *Arnold et al.* [1994], i.e., about 0.3-0.35 as determined from their Figure 2. These large discrepancies, which cannot be attributed solely to differences in aircraft types and which may affect the acid concentration by a factor of about 30, appear to be the major source of uncertainty.

To incorporate the preceding uncertainties, we initialize the H_2SO_4 number densities at values ranging from 10^8 to $10^{12}/cm^3$ at 0.1 s after the exit plane of the nozzle (see caption for Figure 2). These 4 orders of magnitude variation will cover the differences in sulfur fuel concentration, conversion rate of SO_2, and dilution factors. The concentration $10^{10}/cm^3$ corresponds approximately to an emission index of 1 g/kg for SO_2, which in turns corresponds to about 500 ppm of sulfur per kilogram of fuel, the internationally maximum accepted value being 3000 ppm. In addition, the dilution factor used in the AERONOX program has been incorporated to provide the time variation of the acid concentration shown in Figure 2.

Combining the data shown in Figure 1 (temperature and saturation ratio for water) with the number concentrations for H_2SO_4 shown in Figure 2, we obtain the rate of nucleation as a function of plume age (along the centerline) assuming both steady state (equation (11)) and nonsteady state (equation (12)) binary nucleation theory. These calculations, shown in Figure 3, include hydrate formation. Calculated hydrate distributions show that about 99.99% of the acid molecules are hydrated with the overwhelming majority of these being in the monohydrate form. From Figure 3 one can see that from the highest to the lowest acid

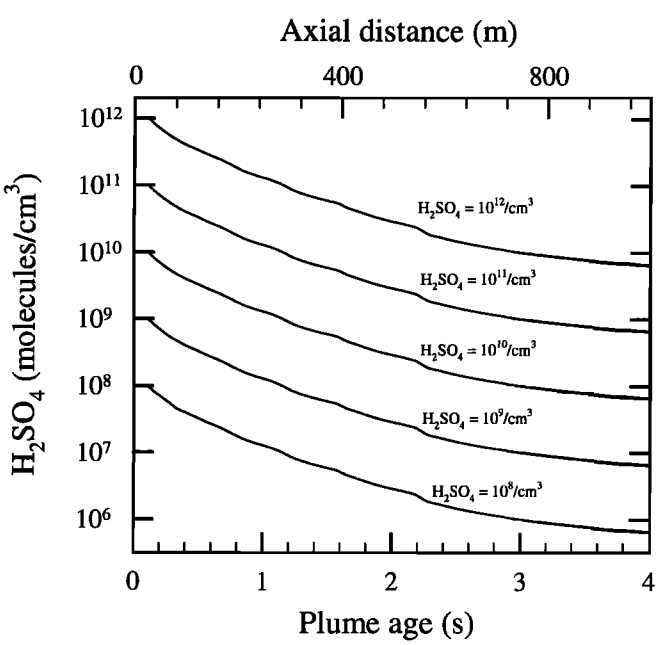

Figure 2. Evolution of the sulfuric acid number densities as a function of plume age (or axial distance) in the wake of a B767 jet engine. The labels in the figure correspond to the initial number densities (10^8 to $10^{12}/cm^3$) assumed to exist 0.1 s after the exit plane of the nozzle.

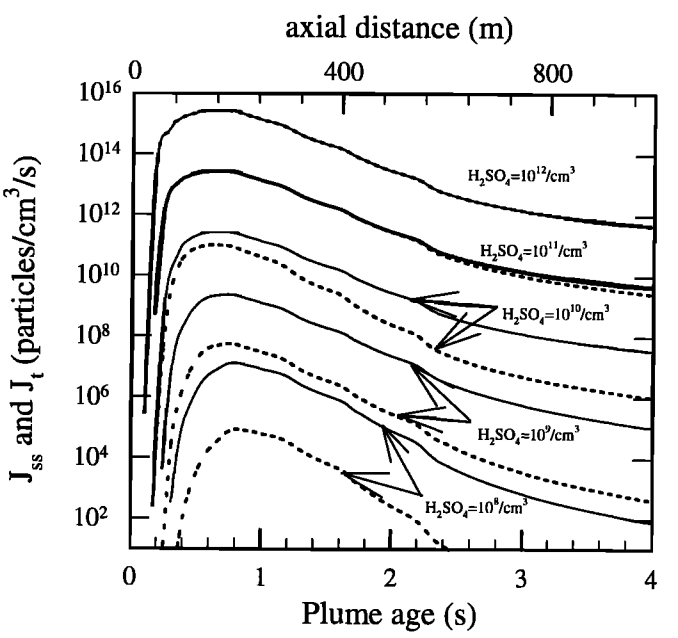

Figure 3. Homogeneous H_2O-H_2SO_4 nucleation rates as a function of plume age (or axial distance) in the wake of a B767 jet engine. Solid curves, steady state rate J_{ss} from equation (11); dotted curves, nonsteady state rate J_t from equation (12). The labels in the figure correspond to the initial number densities of H_2SO_4 assumed to exist 0.1 s after the exit plane of the nozzle. Note superposition of the solid and dashed curves at the highest acid number density ($10^{12}/cm^3$).

Table 1. Steady State Nucleation Rates J_{SS}, Time Lags τ and Inverse of the Collision Frequencies

Case	H_2SO_4 Number Densities, molecules/cm^3	J_{SS} (Maximum Nucleation Rate Including Hydrates), particles/cm^3/s	Time lag τ, s	$1/\nu_j^*$, s
1	10^8	1.3×10^7	125	141
2	10^9	2.3×10^9	11.1	13.8
3	10^{10}	2.6×10^{11}	1.2	1.4
4	10^{11}	2.6×10^{13}	0.09	0.10
5	10^{12}	2.6×10^{15}	9.04×10^{-3}	1.03×10^{-2}

loading considered, nucleation occurs after 0.1 to 0.3 s (i.e., 25 to 75 m); the predicted nucleation rate passing through a maximum at about 0.6 to 0.9 s (i.e., 150 to 225 m) and then decreasing. A more realistic model would include particle growth, which would lead to an even more rapid decrease in the nucleation rate due to the additional depletion of acid molecules through condensation. These findings are in good agreement with the recent study of *Kärcher et al.* [1995], who, including growth and gas-phase depletion, found that the nucleation period, assuming steady state nucleation, is limited to a period of 0.2-1 s after exhaust from the engines.

In Table 1 we present the calculated time lags corresponding to the maximum rates for the different initial number densities of acid listed in Figure 2. For example, in case 1 (lowest acid loading) a rather large nucleation rate (steady state) of 1.3×10^7 particles/cm^3 is predicted to occur after 0.8 s, but a transient period of about 125 s would be necessary to achieve this rate. As a result, appreciable nucleation will start much later than 0.8 s, leading in turn to much lower rates, since after 125 s, dilution will have reduced both the saturation ratio of water and the acid concentration. As the number density of H_2SO_4 increases (cases 2 through 5), the time lag is reduced. This behavior is expected, since the time lag depends on the collision frequency of acid molecules (or hydrates) with the *i,j* clusters. As can be seen in Table 1, there exists a good correlation between the calculated time lag and the inverse of the collision frequencies $1/\nu_j^*$ with the cluster of critical size. Only for cases 4 and 5 (highest acid loading) are the time lags (0.09 s and 9×10^{-3}) short enough that the steady state assumption yields acceptable particle nucleation rates.

Conclusion

Steady state rates and time lags for binary homogeneous nucleation were examined for a subsonic aircraft flying near the tropopause, under conditions for which no visible contrail is expected to form, i.e., maximum relative humidities in the wake below 100%. Except at the highest acid loading considered the wake conditions were found to be such that the time lags for nucleation exceeded the timescale (shown in Figure 3 to be of the order of 1 s) during which the most favorable nucleation conditions are reached in the plume. As a result the steady state assumption is generally not valid, and equation (11) cannot be used to estimate the nucleation rate. Time-dependent cluster populations can be obtained within the framework of the binary theory by direct integration of equation (8) for time-dependent matrix K and vector a or, equivalently, from integration of equation (7). Such detailed calculations, which are beyond the scope of the present study, will likely be most useful at intermediate acid loading (such as case 3 of Table 1), where the time lag is comparable to the plume age for which the most favorable nucleation conditions are reached. Nonsteady state nucleation rates can also be estimated through the use of approximations such as equation (12). Using the latter approach, we obtain the results shown by the dashed curves in Figure 3.

The matrix method described here utilizes the physically motivated approximation that clusters establish rapid equilibrium with the more abundant water vapor species present in the wake. This quasi equilibrium approximation [*Shugard et al.*, 1974; *Schelling and Reiss*, 1981a], which was shown to be quantitative under atmospheric conditions [*McGraw*, 1995], greatly reduces the dimensionality of the matrix. In the present calculations this reduction ranges from the order of 600, corresponding to the total number of binary cluster combinations containing up to 6 acids and 100 waters, to the order of 6, corresponding to the maximum number of acids in a cluster. The time lag was computed as the reciprocal of the smallest eigenvalue of H rather than by the variation method, which yields only a lower bound for this quantity. As a further check on the present calculations we have verified that the lowest eigenvalue and remaining eigenvalues of H are in quantitative agreement with the smallest eigenvalues of the full two-dimensional kinetics matrix under conditions for which the complete eigenvalue distribution of this very large matrix (of the order of several thousand) was obtained by other methods [*McGraw*, 1995]. These smallest eigenvalues, which govern the longtime relaxation behavior associated with the gain and loss of sulfuric acid molecules in the fully binary calculations [*McGraw*, 1995], are therefore projected out directly from the reduced K matrix of equation (9) derived by using the quasi equilibrium assumption.

Although the above calculations apply to wakes in which the saturation ratio of water never exceeds unity, by slightly changing the conditions, e.g., by increasing the relative humidity of the background atmosphere, the wake can become supersaturated with respect to water vapor, leading to the formation of "visible" contrails. In such cases these contrails form about 0.3-0.4 s behind the engines and may result from heterogeneous condensation on engine soot as well as on the sulfuric acid-water aerosol. Depending upon the concentration of sulfuric acid in the wake (which in turn depends on the sulfur content of the fuel), appreciable production of aerosols will or will not precede the formation of "visible" contrails. According to our calculations, if the concentration of H_2SO_4 is of the order of 10^{11}-10^{12}/cm^3, the time lag effect is negligible, and a very high production of aerosols will occur first in the wake. The number density of the newly formed aerosol will exceed the number density of soot particles (the latter of the order of 10^7/cm^3) and therefore can influence the properties of the contrail particles (number

densities), which form slightly later. These predictions seem to be qualitatively in good agreement with the observation of *Schumann et al.* [1996]. If, on the contrary, the acid concentration is much lower (10^8-10^9/cm^3), the aerosol is still generated first, but at a much lower rate. The number of newly formed aerosols may then be too small to compete with the activation of the soot particles during visible contrail formation. Again this conclusion seems to be (qualitatively) in good agreement with the observation of *Busen and Schumann* [1995]. Additional modeling studies, which specifically address the competition between soot particles and homogeneously nucleated sulfuric acid-water aerosol (to serve as CCN under supersaturated water conditions), are necessary for a more complete comparison between experimental observation and theoretical predictions.

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