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# Particle Processes in Aircraft Plumes

by

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# PARTICLE PROCESSES IN AIRCRAFT PLUMES

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**Abstract.** The formation of new particles in aircraft exhaust plumes is reviewed. The emission characteristics of soot particles and the nucleation of ice particles in contrails are also discussed. Physical interactions between the newly formed particles, the soot particles, and the contrail ice particles in the expanding and cooling plume are elucidated.

## 1. INTRODUCTION

The objective of this lecture held during the ASTAIRE Summer School was to summarize the state of knowledge of particle formation and interaction processes occuring in aircraft exhaust plumes. Aspects of plume dynamics and gas phase chemistry were discussed only as far as they concerned particle formation processes behind the aircraft. Soot and contrail ice particles were addressed only in relation to their interaction with the newly formed, volatile particles.

The balloon-borne observations of Hofmann and Rosen [1978] first suggested the formation of new aerosols behind aircraft, presumably resulting from binary homogeneous nucleation of $H_2SO_4$ and $H_2O$, in addition to emitted, solid soot particles. In the early 1990s, it was conjectured that the greatest particle formation probability has to be expected in the nascent jet plume, because only there are the gas concentrations and mixing/cooling rates large enough to trigger a phase transition in the turbulent jet flow [Miake-Lye et al., 1993].

During the past 6 years, significant progress has been made towards an understanding of how the new particles come about. Through the fruitful cooperation between theoreticians and experimentalists performing field and laboratory studies, we now have a relatively clear conceptual picture of the formation and growth of ultrafine particles in aircraft plumes, although uncertainties in their chemical composition, their heterogeneous reactivity, and their fate in the atmosphere still exist.

The content of this contribution is guided, in part, by a recent evaluation of this topic in the special report "Aviation and the Global Atmosphere" published by the Intergovernmental Panel on Climate Change [IPCC, 1999; Chapter 3.2]. For students who wish to study this subject in greater detail, I refer to a review article published recently [Kärcher, 1999]. The present contribution summarizes the knowledge on this issue using additional information that became available until mid-1999.

## 2. PLUME DYNAMICS

Exhaust gases from aircraft are introduced into the atmosphere in the form of coflowing jets. The exhaust jets emanating from the nozzle exit planes of the engines are trapped in two expanding vortices originating from the wingtips of the airplane [Miake-Lye et al., 1993; Gerz et al., 1998]. During the first seconds after emission (jet regime), the jet plumes spread up but remain isolated. This stage is characterized by rapid cooling of the exhaust from $400 - 600\,\mathrm{K}$ to atmospheric temperatures ($< 230\,\mathrm{K}$), and by a concomitant dilution of the exhaust products due to turbulent mixing with background air. The jet regime is most important for the discussion of new particle formation below. The following vortex regime lasts $2-3$ minutes and is terminated by turbulent dissipation. It is characterized by slower dilution at nearly constant temperatures.

Inhomogeneities induced by turbulence directly translate into pronounced variabilities of meteorological parameters and species abundances on temporal scales $\sim 1$ s and spatial scales $\sim 1$ m [Baumgardner et al., 1998]. Also, because temperature and mixing evolves differently along the individual streamlines of the flow field, the results of chemical and microphysical processes (which sensitively depend upon these parameters) can differ depending on the location in the wake. Often, this complicates the evaluation of measured data and comparisons with model results.

## 3. PLUME CHEMISTRY

Chemical reactions that take place in the jet regime set the stage for the subsequent chemical evolution up to the global scale. They determine which fractions of the primary emissions (NO, $NO_2$, $SO_2$, $SO_3$) are transformed into higher oxides (e.g., $HNO_3$, $H_2SO_4$). Since these secondary species are potential aerosol-forming species (precursors), they affect ozone indirectly via heterogeneous chemical reactions involving the particles they have formed.

### 3.1. SULFUR CHEMISTRY

The fuel sulfur (S) content in aviation fuels (kerosene) varies from 1 ppm to 3000 ppm by mass, with an average near 500 ppm or 0.5 g S per kg fuel. Most of the fuel S is emitted as $SO_2$. A fraction of the $SO_2$ is converted into fully oxidized S species ($= SO_3 + H_2SO_4$) by gas phase chemical reactions with hydroxyl radicals (OH), oxygen atoms (O), and $H_2O$ on the way from the combustor into the aircraft plume [Lukachko et al., 1998; Tremmel and Schumann, 1999]:

$$\mathrm{SO_2 + OH} \xrightarrow{\mathrm{M}} \mathrm{HSO_3} \tag{1}$$

$$\mathrm{HSO_3 + O_2} \longrightarrow \mathrm{HO_2 + SO_3} \tag{2}$$

$$\mathrm{SO_2 + O} \xrightarrow{\mathrm{M}} \mathrm{SO_3} \tag{3}$$

$$\mathrm{SO_3 + n \cdot H_2O} \xrightarrow{\mathrm{M}} \mathrm{H_2SO_4 \cdot (H_2O)}_{n-1}\,. \tag{4}$$

The rate coefficients of these reactions in the gas phase depends on details of the combustion and plume kinetics, turbine flow properties and blade cooling effects, and mixing in the jet. In the OH-induced oxidation sequence, reaction (1) is the rate limiting step. Once $SO_3$ is formed via (2), the reaction (4) with emitted $H_2O$ to form $H_2SO_4$ is fast ($< 0.1$ s) under plume conditions. The chemical lifetime of exhaust OH in the early jet regime (a few milliseconds) is determined by gas phase reactions with emitted NO and $NO_2$, and by OH self-reactions, leading to the formation of $HNO_2$, $HNO_3$, and hydrogen peroxide ($H_2O_2$) [Kärcher et al., 1996], all of which are water-soluble species. Recent studies suggest that most OH formed from combustion is consumed, mainly by reactions with NO, already before the exhaust gases reach the engine exit. OH is reformed later in the wake by photolysis of $HNO_2$ [Hanisco et al., 1997].

Direct emissions of $SO_3$, mainly formed via the O-induced oxidation of $SO_2$, markedly increase the $H_2SO_4$ concentration in the plume. The amount of $SO_3$ present at the nozzle exit plane is mostly generated within the jet engines and is linked to details of the combustion kinetics and depends on the engine design. Aerosol formation and growth rates are extremely sensitive functions of the fraction of S converted to $SO_3$ and $H_2SO_4$ at emission [Brown et al., 1996; Kärcher and Fahey, 1997]. Sulfur dioxide and higher S oxides have been detected in jet plumes of commercial aircraft [Miake-Lye et al., 1998; Curtius et al. 1998].

### 3.2. CHEMI-IONS AND ORGANICS

A large number of chemi-ions are present in aircraft exhaust since ion production via chemical ionization reactions occurs in the combustion of carbon-containing fuels. Positive ions are mainly light organic molecules, whereas free electrons rapidly attach to $O_2$ which in turn reacts with nitrogen and sulfur species to form the stable ions $NO_3^-$ and $HSO_4^-$. These negative ions further attract polar molecules such as $HNO_3$ and $H_2SO_4$ to form larger charged molecular clusters.

Chemi-ions have been detected on the ground and in flight [Arnold et al., 1998; 1999]. During the latter field observations, very massive negative ions have been observed, indicating that the initially molecular-sized clusters quickly grow by uptake of condensable species. This observation strongly supports the idea that exhaust chemi-ions promote the formation and growth of electrically charged $H_2SO_4/H_2O$ droplets [Yu and Turco, 1997], likely also containing organic exhaust species [Kärcher et al., 1998a]. Comparisons with particle measurements in plumes and calculations based on ion-ion recombination kinetics suggest the presence of $10^9\,\mathrm{cm}^{-3}$ or more chemi-ions at the engine exit planes, corresponding to at least $10^{17}$ ions per kg fuel. There is no indication that the production of chemi-ions is linked to the fuel S content.

Under flight conditions, methane is the most abundant hydrocarbon (HC) in the exhaust. Few measurements of non-methane hydrocarbons indicate significant plume concentration enhancements of alkenes (mostly ethene), aldehydes (mostly formaldehyde), alkines (mostly ethine), carbonyl compounds, and a few aromates. Many of them could condense on the sulfate aerosols formed in the young plume, as suggested by an analysis of ultrafine particle measurements in cases where kerosene with unusually low S contents (below about 50 ppm by mass) has been used [Kärcher et al., 1998a; Yu et al., 1998].

## 4. PLUME AEROSOL TYPES AND INTERACTIONS

The following aerosol types have been identified by in situ observations in aircraft exhaust plumes: (1) Liquid aerosols that mainly consist of $H_2SO_4$ and $H_2O$, resulting from homogeneous nucleation. Part of these aerosols originate from emitted chemi-ions and carry an electrical charge. (2) Non-volatile combustion aerosols that are mainly composed of black carbon soot, and to a lesser extent, of metallic particles. The soot particles very likely acquire a liquid surface coating in the jet plume by interaction with sulfur gases and $H_2SO_4/H_2O$ droplets. (3) Ice particles formed via freezing nucleation in contrails that rapidly take up the emitted $H_2O$ in an initial growth stage.

Figure 1 is a schematic of the physico-chemical processes that take place in aircraft plumes. Some aspects of the plume chemistry have been addressed above. In what follows, I discuss several of the microphysical processes while explaining the key characteristics of the different particle types present in exhaust plumes.

# 5. NEW PARTICLE FORMATION

Figure 2 is a schematic showing the size distributions of the different plume particle types at a plume age of 1 s as inferred from measurements and models. In the diameter range below 10 nm, the overall number size distribution is dominated by the volatile nucleation mode containing particles mainly composed of $H_2SO_4$ and $H_2O$ (for fuel S contents above average values).

Models suggest that the volatile particle size distribution may actually exhibit a bimodal structure [Yu and Turco, 1997]. Very recently, it became possible to directly measure the ultrafine particle size distribution above 3 nm diameter using a suite of condensation particle counters. Together with previous observations, these measurements strongly support the following picture of new particle formation in young exhaust plumes [see Yu et al., 1999].

## 5.1. FORMATION PROCESSES

The smaller particles are formed by aggregation of homogeneously nucleated clusters of hydrated $H_2SO_4$ molecules (neutral mode). The larger particles are formed by rapid scavenging of small molecular clusters by chemi-ions (ion-mode). The growth of charged particles is preferred over the growth of neutral particles due to a net enhancement of the condensation and coagulation rates in a charged aerosol.

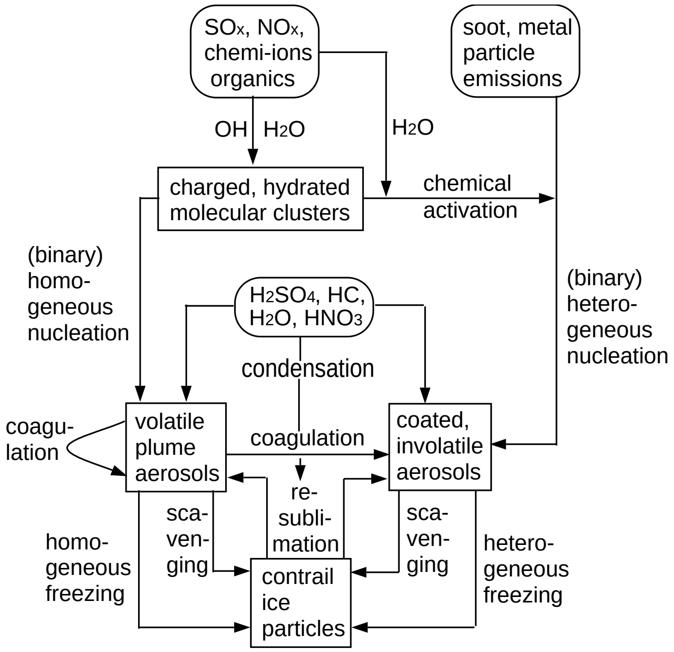

**Fig.1:** *Schematic of aerosol dynamics and related chemistry in aircraft exhaust plumes and contrails. Round and rectangular boxes denote species emitted and formed in situ, respectively. The arrows and corresponding labels indicate transformation processes that are described by current simulation models.*

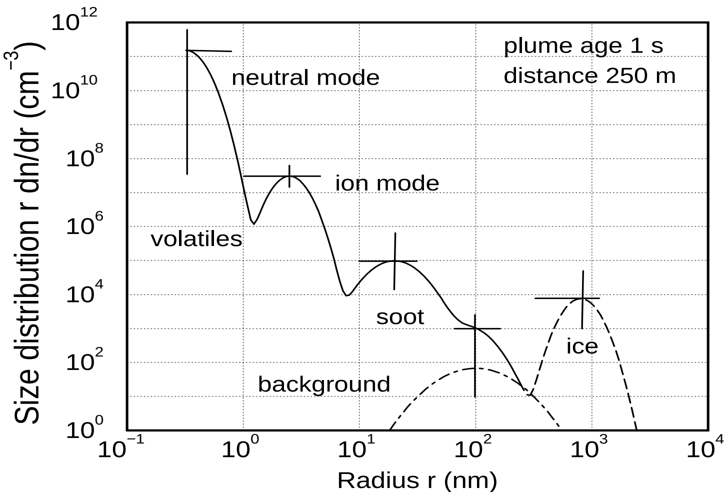

**Fig.2:** *Size distributions of the particle types present in aircraft exhaust plumes. If a contrail forms, these sepctra change (not shown) and ice particles are created (dashed curve). Bars denote variabilities of the respective parameters. A background spectrum (dot-dashed curve) is shown for comparison.*

The concentration of cluster-particles in the neutral mode depends strongly on the fuel S content. Their mean size is relatively invariant owing due imperfect sticking of hydrated $H_2SO_4$ clusters after a collision. The mean size of the ion mode particles depends on the amount of material available for condensation. The concentration of the order $10^{17}$ ionized particles per kg fuel burnt is relatively invariant, indicating that they nucleate on virtually all of the chemi-ions formed within the jet engine.

Besides $H_2SO_4$, which preferably condenses onto negative ions, organic exhaust species mainly condense onto positively charged clusters owing to their relatively large proton affinity. This implies that the ion mode actually consists of at least two modes (not resolved in Figure 2), and may contain, besides $H_2SO_4$ and $H_2O$, exhaust hydrocarbons.

## 5.2. LINK TO SULFUR CHEMISTRY

Until recently, it was hypothesized that jet engines may emit much larger amounts of $SO_3$ and $H_2SO_4$ (together referred to as S(VI)) than previously believed, revealing a basic discrepancy between models and observations. Because of the strong sensitivity of nucleation and growth of volatile particles to emitted S(VI), understanding of $SO_3$ formation in jet engines is an essential prerequisite in controlling these aerosols [Kärcher and Fahey, 1997].

At this time, conversion fractions of fuel S to S(VI) in the engine of 20 % or more seemed necessary to model observed new particle formation in aircraft plumes in some cases; see compilation in Kärcher [1999]. However, chemical models designed to calculate S chemistry in the engine and nascent plume only predicted at most $5-15\,\%$ conversion; see above. Relating S conversion to the amount and size of newly formed particles requires the use of detailed microphysical simulation models. While such models confirm the observed properties of volatile particles, as well as their overall dependence on the fuel S content, no systematic comparison has been performed to date.

One key to resolve the open question of S conversion could be the emission of organics and their participation in the particle formation and growth process. It has been noted that a small amount of exhaust hydrocarbons being present in the ultrafine particles removes the necessity of assuming high ($> 10\,\%$) S conversion rates [Kärcher et al., 1998a].

In one observed case, where fuel with a low S content was used (20 mg S per kg fuel), the incorporation of emissions of 23 mg/kg of condensable organics into a plume model including the effect of chemi-ions reduced the S-to-S(VI) conversion fraction prescribed in the model to simulate the measurements from 55 % to only 10 % [Yu et al., 1999]. Interestingly, the observations could not be explained when chemi-ion emissions were neglected in the model; the same holds for measurements performed with very rich S fuel [Yu et al., 1998]. On the other hand, for sufficiently high S emissions, the abundance of $H_2SO_4$ in the plume is adequate to dominate particle growth, thus rendering unimportant the comparatively low organic mass in the exhaust.

## 5.3. FATE IN THE ATMOSPHERE

In the absence of contrails, in which case the plume never becomes supersaturated with respect to water, the newly formed particles grow and shrink as a function of relative humidity. They stay in local equilibrium with gaseous $H_2O$. The $H_2SO_4$ molecules that entered the droplets during nucleation stay in the liquid phase due to their very low saturation vapor pressure.

Because it is not yet clear which organics from the exhaust are involved in new particle formation and growth, the fate of the particulate organic matter in the atmosphere is unclear. Simulations show that the $H_2SO_4/H_2O$ particles may also take up $HNO_3$ in the near field [Kärcher et al., 1998b]. While the dissolved $HNO_3$ may persist in sufficiently cold and $HNO_3$-rich stratospheric air, it is only short-lived ($< 1\,\mathrm{min}$) under typical upper tropospheric conditions.

The volatile particles formed in the plume may be too small to act as as efficient cloud condensation nuclei (CCN) or ice forming nuclei (IN) later, unless the air mass containing the aerosol is lifted or cooled or becomes relatively more humid. They grow slowly by cogaulation; condensation of ambient $H_2SO_4$ and perhaps other material may accelerate the growth rates. However, detailed observations of the microphysical and chemical evolution of these particles from the plume to the global scale are lacking. This represents an important uncertainty in assessing their potential global impact on chemistry and cloud formation.

## 5.4. PERTURBATION OF AMBIENT PARTICLES

Aircraft flying through a specified region in the atmosphere continuously emit new particles into this volume. These new particles add to the existing background aerosols. On the other hand, scavenging by background aerosols is the most likely fate of the small new volatile particles; see also Figure 1. Neglecting to a first order transport processes of particles from neighbouring regions, one may imagine that a quasi-steady state concentration of aircraft-produced aerosols develops in that region. Let us examine the magnitude of this perturbation on a regional scale in terms of the relative increase of the total particle surface area. For simplicity, we only consider sulfate aerosols at this point.

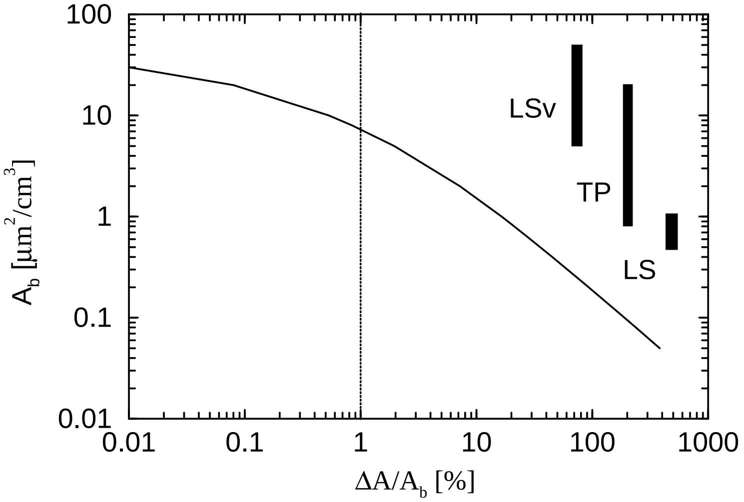

**Fig.3:** *Perturbation of the background aerosol layer versus background aerosol surface area density. The bars indicate the range of variability of $A_b$ in the lower stratosphere under non-volcanic (LS) and volcanic (LSv) conditions, and in the tropopause region (TP). Perturbations to the left of the vertical line are considered negligible.*

Consider a fleet of aircraft in the North Atlantic flight corridor (NAFC). The cross-section of the NAFC is roughly $2000\,\mathrm{km}^2$ and extends about 2 km in the vertical, centered around the average cruising altitude. Around 800 subsonic planes cross that volume per day (1998 figure); similar numbers can be expected by a large fleet of planned supersonic aircraft. Based on a description of particle coagulation processes in the decaying plumes, Kärcher and Meilinger [1998] estimated the steady-state perturbations of the sulfate aerosol surface area density. Figure 3 illustrates the perturbations (relative to the background value) in the NAFC as a function of the existing aerosol surface area density.

The graph shows that the perturbations can be significant ($> 10\,\%$) whenever the background particle surface concentration falls below about $2\,\mu\text{m}^2/\text{cm}^3$, which is certainly the case at the supersonic flight levels in the lower stratosphere, and may at times occur in the tropopause region. These numbers are supported by a statistical analysis of ballonborne CN data [Hofmann et al., 1998] and by estimates using a suite of global transport models [Danilin et al., 1998]. The latter authors also show that comparable aircraft-induced perturbations can be expected for soot particles.

## 6. SOOT PARTICLE EMISSIONS

Aircraft jet engines directly emit solid soot particles. The term soot encompasses all primary, carbon-containing products from incomplete combustion processes. Besides the pure (optically black) carbon fraction, these products may also contain non-volatile (gray) organic compounds. Exhaust soot is important in providing nuclei for liquid drop or ice crystal formation; soot strongly absorbs radiation and potentially affects air composition.

### 6.1. PARTICLE CHARACTERISTICS

Soot emissions depend on engine types, power settings, flight levels, and possibly on the state of engine maintenance. The recent IPCC report [1999] gives a mean average soot emission index of 0.04 g soot per kg fuel for the present subsonic fleet. Older jet engines emitted up to 1 g/kg. No significant dependence exists between soot emission index and fuel S content. Figure 4 shows electron photographs of soot and $H_2SO_4/H_2O$ particles from in situ measurements, revealing the irregular structure of the larger soot particles (agglomerates).

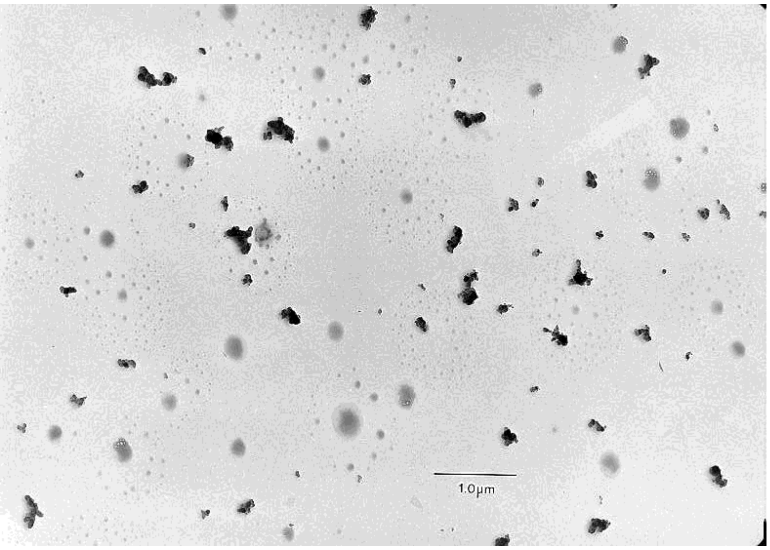

**Fig.4:** *Exhaust particles in the plume of an F-16 aircraft in flight. Photomicropgraph taken with a transmission electron microscope. Soot and aqueous sulfuric acid particles (seen as faint spherical droplets) are visible in this sample, and sulfur has been detected in/on some of the soot particles suggesting soot and sulfur interaction occuring in young plumes. The large sulfate droplets are background particles entrained into the plume. Figure by P. Sheridan downloaded from the web site:* `www.cmdl.noaa.gov/aerosol/about/sheridan/particles.html`.

Petzold et al. [1999] have recently compiled size distributions, microphysical and optical properties, and emission indices of soot particles measured behind a different jet engines. The results seem to support the presence of two soot modes (as those shown in Figure 2), a primary mode with a mean diameter of 30 nm and a mode of agglomerated primary soot particles at 150 nm, with at least two orders of magnitudes differences in number concentrations. The fine black carbon particles seem to dominate light extinction of the plume aerosol (soot particles are very efficient light absorbers).

These data indicate, at least for the aircraft types considered, that modern engines emit less soot particles by mass and number, and that the particles are somewhat smaller than those from old-technology engines. This is an interesting similarity to the emission trends observed of soot from motorcars.

### 6.2. HYDRATION PROPERTIES

Soot particles fresh from jet engines very likely become hydrophilic due to activation by deposition of $H_2O$ molecules and water-soluble species present in the exhaust, starting in the jet regime and perhaps even within the engines. Irregular surface features can increase the adsorptivity and amplify nucleation processes. It is known that soot hydrates more effectively with increasing fuel S content [Hagen et al., 1992]. For average and high S levels, $H_2SO_4$ is likely the primary soluble constituent on soot surfaces.

Production of soluble material by soot and $SO_2$ interaction is only possible by assuming perfect sticking of $SO_2$ molecules and rapid heterogeneous conversion to sulfate on the carbon surfaces. However, sticking probabilities of gaseous $SO_2$ on amorphous carbon are too small to lead to significant surface coverages and time scales in young exhaust plumes seem too short to allow heterogeneous $H_2SO_4$ production. However, $SO_3$ and $H_2SO_4$ molecules might easily adsorb on soot prior to volatile particle formation, and direct emissions of S(VI), as suggested by recent observations, may explain the measured soluble mass fractions on soot. Scavenging of small volatile droplets constitutes another soot activation pathway.

### 6.3. FATE IN THE ATMOSPHERE

The liquid $H_2SO_4/H_2O$ coating resulting from the above-mentioned interaction between soot and freshly formed sulfur particles increases with the plume age and may enhance the ice forming ability of soot (see next section). In the aging plume, a mixed soot/sulfate aerosols forms. Additionally, the pure and coated soot particles will be scavenged by ambient aerosol particles on the time scale of days (see Figure 1), constituting an important sink of exhaust soot.

## 7. CONTRAILS

The formation of contrails is due to the increase in relative humidity that occurs during the mixing of the warm and moist exhaust gases with the colder and less humid ambient air. A contrail will form when saturation with respect to liquid water is reached in the plume.

The thermodynamic relation for contrail formation requires knowledge of the air pressure, temperature, and relative humidity at a given flight level, and fuel properties such as the emission index of $H_2O$, the combustion heat, and the overall aircraft propulsion efficiency. The thermodynamic criterion linking these parameters is well-established and verified by in situ observations. For more details, I refer to the contribution “Observations, distributions, and radiative impact of contrails” by Ulrich Schumann in this volume.

## 7.1. PROPERTIES OF CONTRAIL ICE PARTICLES

Young contrails consist of ice particles that nucleate primarily on exhaust soot and volatile aerosol particles. Contrails become visible within roughly a wingspan distance behind the aircraft, implying that the ice particles form and grow large enough to become visible within the first tenths of a second. A lower limit concentration of $10^4\,\mathrm{cm}^{-3}$ particles emitted or formed in the plume is necessary for a contrail to have an optical depth above the visibility threshold. The corresponding mean radii of young contrail ice particles are around $0.5 - 1\,\mu$m; see Figure 2.

Numerical simulations, partly supported by observations, suggest the following features [Kärcher et al., 1998b]. Contrail ice particle number densities (mean sizes) increase (decrease) with falling temperatures and rising fuel S content. However, contrail properties do not strongly depend on the level of sulfur in the plume because ice formation and growth is a self-limiting process and depletion of gaseous $H_2O$ prevents further nucleation when the concentration of ice particles exceeds $\sim 10^5\,\mathrm{cm}^{-3}$.

The particles in contrails formed within thin cirrus clouds are different from those formed in clear air, possibly due to the additional $H_2O$ provided by the ice crystals. Thus, the evolution of cirrus clouds can potentially be modified by aircraft exhaust. Contrails would also form without soot and S emissions by activation and freezing of background particles. However, the resulting contrails would have different microphysical properties.

As noted above, exhaust particles which grew to larger sizes froze and consititute the major part of the contrail ice mass. Ambient aerosols may play a larger role in contrail regions that nucleated at the plume edge where the ratio of ambient to soot particles is largest and when ambient temperatures are low [Jensen et al., 1997] or in the upwelling limbs of the vortices [Gierens and Ström, 1998]. Metal (and soot) particles have been found as inclusions in contrail ice particles larger than $2 - 3\,\mu$m in radius [Twohy and Gandrud, 1998]. However, they are numerically unimportant compared to the other plume aerosols. In this large size mode mineral components also have been detected, indicating the contribution of ambient particles to ice formation in contrails.

## 7.2. FREEZING MECHANISMS

Both homogeneous and heterogeneous freezing processes are possible in contrails. The most efficient freezing mode takes up the available (emitted) $H_2O$ and prevents growth of other particle modes.

Soot is expected to play an important role in the formation of contrails at and down to a few K below the threshold formation temperatures. Contrails observed under such conditions are explained to result from freezing of ice within water-activated soot particles. Volatile droplets are then prevented from freezing because the freezing of soot-containing particles is too rapid.

Fresh soot particles do not act as efficient ice deposition nuclei in the exhaust because their surfaces are not well suited to initiate the direct gas-to-solid (ice) phase transition. This follows from the absence of contrails at temperatures above the liquid water saturation threshold.

Water activation of soot may result from the formation of at least a partial coating of the soot surfaces with aqueous $H_2SO_4$; see above. Prior to contrail formation, this surface coverage increases with the fuel S content and leads to a greater number of ice particles. The acid coating will persist at the soot particle surfaces. Figure 5 sketches the heterogeneous freezing pathway leading to contrails.

Contrails at threshold conditions are also observed when very low (2 ppm by mass) fuel S is used [Busen and Schumann, 1995]. This amount of S leads to $H_2SO_4$ surface coverages of only 0.02 % [Kärcher et al., 1998b], which raises the question whether the soot activation by sulfur gases supports heterogeneous freezing in such cases. This may point towards the formation of a pure water coating (dashed arrow in Figure 5) that is enhanced when the fuel S level is increased to average values or higher. Such a process could explain the observed insensitivity of contrail formation and visibility to changes of the fuel S content for very low sulfur levels. The formation of a (partial) liquid $H_2O$ coating may be facilitated by both physical (adsorption due to an inverse Kelvin law effect in concave surface features) and chemical (hydrolyzable, oxygen-containing functional groups and other polar adsorption sites to which water molecules are bonded) mechanisms.

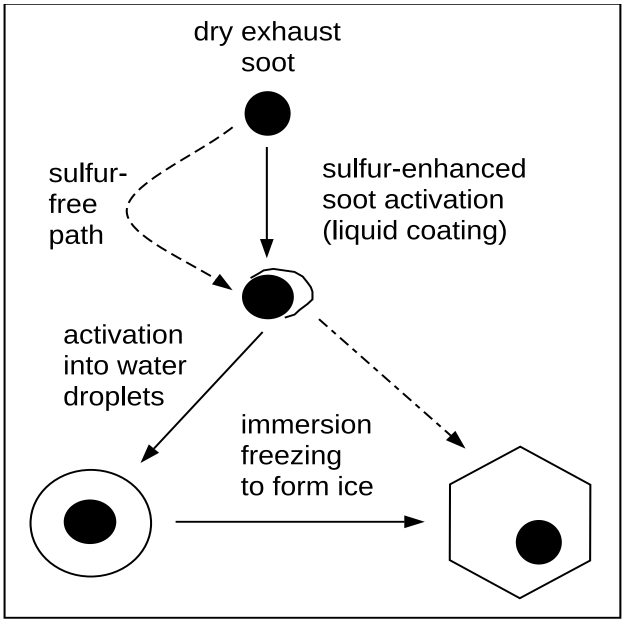

**Fig.5:** *Schematic showing the soot-induced freezing pathway leading to contrails. Soot particles acquire a (partial) liquid coating of $H_2SO_4$ and $H_2O$ due to adsorption of oxidized sulfur gases and scavenging of volatile droplets. They also trigger freezing if the fuel S content is very low (a few ppm by mass), suggesting an additional sulfur-free heterogeneous freezing mode (dashed arrow). Few ice particles may also nucleate without water activation (dot-dashed arrow). Soot dominates ice formation at and slightly below threshold formation temperatures. Homogeneous freezing may also occur and enhance the ice mass for lower temperatures and/or higher fuel S contents (not shown). Ice crystal shapes are close to spherical in young contrails, but may vary in aging contrails as indicated by the hexagon. Soot cores may reside inside the crystals, or are attached at their surface.*

The mechanism of heterogeneous ice formation via liquid coatings on soot is mainly inferred indirectly from the observations and needs experimental confirmation. Unique evidence that soot is involved in ice formation is difficult to obtain from in situ measurements, because it is difficult to distinguish whether a soot particle caused freezing or whether it was scavenged by an ice particle that formed from homogeneous freezing.

The fraction of activated volatile $H_2SO_4/H_2O$ droplets that freezes depends on the droplet composition (affecting homogeneous freezing rate), the evolution of $H_2O$ supersaturation, and the possible competition with heterogeneous freezing processes involving soot.

Near threshold conditions, model results suggest that the volatile aerosol fraction does not become large (water-rich) enough to freeze [Kärcher et al., 1998b], and heterogeneous freezing of activated soot particles is plausible and consistent with measurements, as described above. At lower temperatures and higher humidities, freezing of volatile aerosols is predicted to occur and also ambient particles may contribute to ice crystal nucleation. In this temperature regime, ice particle formation is predicted to depend on the fuel S content, $SO_3$ emissions, ambient temperature and humidity, and the assumed ice nucleation properties of soot.

Freshly nucleated $H_2SO_4/H_2O$ droplets larger than the threshold activation size (diameter $> 4-10\,$nm) prior to freezing can be activated into water droplets in the contrail. The threshold activation size and, hence, freezing probability, depends on the maximum supercooling reached in the expanding plume. Decreasing ambient temperature and increasing ambient humidity both lower the threshold size and increase the homogeneous freezing rates. In this regard, volatile particles from the ion mode are more easily activated than those from the neutral mode (compare Figure 2), and, hence, can play an important role in contrail formation.

## 7.3. EFFECT OF CONTRAILS ON PLUME PARTICLES

The evolution of volatile particles in the young plume differs strongly in contrails from conditions in dry plumes. As explained above, part of the volatile particles grow by water uptake and may then freeze. The ice particles grow in surface area due to deposition of $H_2O$ and may scavenge part of the neutral volatile and soot particles. Thus contrails contain fewer of the small particles than dry plumes due to coagulation scavenging [Anderson et al., 1998; Schröder et al., 1998]. After evaporation of the ice crystals, the residual soot and sulfate cores are returned to the atmosphere.

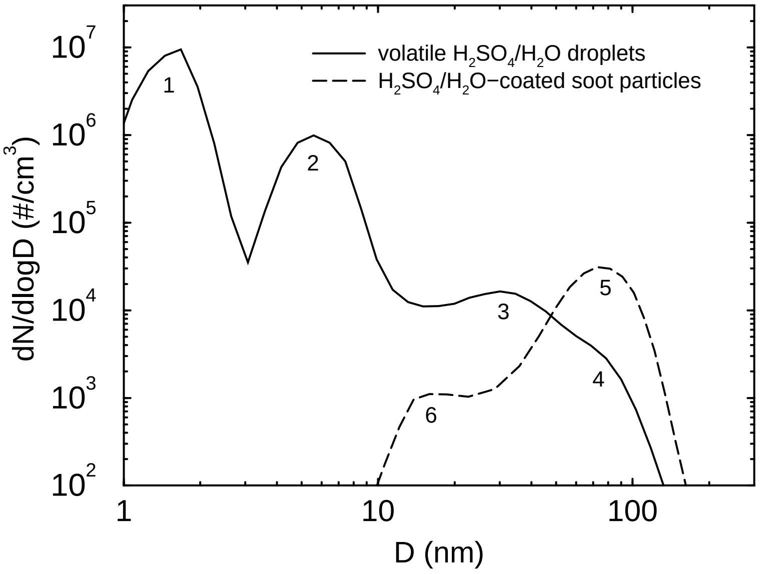

**Fig.6:** *Simulated size distributions of acid (solid curve) and mixed soot/sulfate particles (dashed curve) in an evaporating short-lived contrail in a high sulfur plume at about 20 s plume age. Numbers denote distinct modes in the particle spectra, as explained in the text. Figure courtesy of Fangqun Yu.*

Particle processing in (short-lived) contrails likely leads to a modified aerosol size spectrum and probably composition [Yu and Turco, 1998], similar to the effect cloud processing is known to have on aerosol properties. Figure 6 depicts particle spectra in an evaporating contrail from a simulation model. Both acid and coated soot particle size distributions exhibit distinct modes. Mode 1 and mode 2 represent the neutral and ion mode, respectively, after processing occurred at a plume age of 20 s. Mode 3 at a diameter of $\sim 30\,$nm is an activation mode resulting from water uptake by the largest of the ion mode aerosols; these aerosols did not freeze. Mode 4 at 80 nm is an accumulation-type mode that was processed through the ice crystals, that is, these particles went through a freezing-evaporation cycle. The soot modes 5 and 6 are created analogous to modes 4 and 3, respectively.

### 7.4. FATE IN THE ATMOSPHERE

Observations from space [Minnis et al., 1998] and from in situ measurements [Schröder et al., 1999] clearly show that persistent contrails may develop into cirrus clouds, thereby approaching size distributions as typically observed in young cirrus on time scales of up to a few hours.

Contrail persistence is primarily linked to synoptic conditions that support vertical motions of air, such as frontal zones connected with the warm sector of lows, jet streams that carry moist air across stable highs, and flows induced by mountain waves. These conditions may ensure that the relative humidity exceeds ice saturation, promoting depositional growth of the contrail crystals. Contrail ice crystals evaporate quickly when the ambient air is subsaturated with respect to ice, unless the particles are coated with certain substances such as $HNO_3$ [Diehl and Mitra, 1998].

Soot particles acting as freezing nuclei have the potential to alter cirrus cloud properties [Jensen and Toon, 1997; DeMott et al., 1997]. Although fresh soot particles seem to be poor IN, the present observations do not rule out that aircraft soot particles can act as freezing nuclei with regard to cirrus formation, even without a $H_2SO_4/H_2O$ coating. Information is completely lacking on how the freezing properties of soot change in aging plumes due to interaction with background gases and particles, or due to aerosol processing in contrails.

## 8. SUMMARY

Aircraft jet engines directly emit aerosols and condensable gases which lead to the formation of new, liquid particles in the early plume by nucleation processes. Gas phase species and chemi-ions are also generated in the plume, among which $H_2SO_4$ is of particular importance. Emission and formation of $H_2SO_4$ depend on the fuel sulfur content and the conversion fraction of fuel sulfur to $H_2SO_4$. Nucleation depends, among others, on mixing of the exhaust gases (especially $H_2SO_4$ and $H_2O$) with ambient air, the plume cooling rate, and details of the plume chemistry. Soot particles formed during fuel combustion constitute the major solid (non-volatile) particle fraction present in exhaust plumes. Under certain thermodynamic conditions the emitted $H_2O$ condenses and freezes to water ice particles, thereby forming the contrails. These line clouds may rapidly dissolve when the ambient air is dry. Persistent contrails grow further by deposition of ambient $H_2O$ in an ice-supersaturated atmosphere.

An invisible aerosol trail is always left behind cruising aircraft. Aerosol and contrail formation processes are important because they determine the number, surface area, and mass of particles that are formed per mass of fuel burnt. Exhaust aerosol properties change in the presence of a contrail. Aircraft-induced perturbations of background aerosol surface areas and exhaust aerosol morphology and surface properties are of central importance for ozone changes by heterogeneous chemical reactions. Their number and potential ability to cause freezing are of key relevance for the formation of ice (cirrus) clouds after passage of an aircraft where otherwise no clouds would form. Thereby, aviation-produced aerosols may indirectly influence the radiation budget of the atmosphere.

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