ICE NUCLEATION - A REVIEW

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Abstract -Ice formation in cirrus has been successfully analysed by a number of authors in terms of homogeneous nucleation on dilute sulfuric acid aerosol: laboratory measurements were reconciled with nucleation rates derived from classical theory and field observations support the estimated temperature and humidity regimes at which ice formation is expected. Even so, there is need for further work on this topic. The origin of ice in lower tropospheric clouds is not resolved - it remains a question of great importance and in need of new efforts. In the realm of basic studies, the finding that monolayers and bacterial proteins can be very effective freezing nuclei opened new horizons and may also have implications for atmospheric processes.

Keywords - Homogeneous freezing nucleation. Freezing nucleation by monolayers. Bacterial ice nuclei. Ice formation in clouds.

1. Introduction

The phase transitions of water to ice have crucial consequences in the atmosphere and in biological systems. Studies of the processes even with pure water face many obstacles, and the heterogeneous processes are yet more complex. Improvements in observational and computational methods are producing slow but significant progress. Three topics related to atmospheric ice nucleation will be covered in this review. Two of these - one concerning the lowest temperatures, the other those very close to 0°C - are areas of great scientific activity and significant advances. In the third, the traditional focus of atmospheric ice nucleation research, progress appears quite slow.

2. Upper tropospheric clouds

Cirrus clouds have come into increasing scientific focus over the last decade or so, because of their role in the Earth's radiation budget and climate. Polar stratospheric clouds have been shown to be important participants in the complex chemistry leading to ozone depletion. These concerns brought about renewed interest in homogeneous freezing and in the supercooling of haze particles. New laboratory experiments and field observations were coupled with improvements in theoretical descriptions.

There were no major conflicts in the data accumulated on homogeneous freezing over the

fifty or so years since the first observations that the practical limit to supercooling of water in the laboratory is around -40°C. The dependence of this limit on sample volume has been well demonstrated, and the rate of ice formation was successfully interpreted in terms of nucleation rates (J_{sl}). With rough values for many constants, especially for the interfacial energy between the ice embryo and water, the quasi-thermodynamic theory was reconciled in many slightly different forms with the empirical results. Reviews of work up to about 1990 are in Götz et al. (1991), Pruppacher and Klett (1978) and numerous other texts. These laboratory and theoretical results were also in reasonable accord with observations of rapid glaciation in the tops of deep convective clouds and with the prevalence of ice in cirrus forming at temperatures near -40°C.

More recent work refined the situation in many respects. First, evidence was accumulated supporting the dominance of homogeneous freezing in the formation of cirrus at cold enough temperatures. Second, further laboratory experiments extended somewhat the empirical data base. Third, the possibility was investigated that haze particles (concentrated solution droplets of subcritical size for growth at the prevailing humidities) may freeze directly. Fourth, revisions in the theory of homogeneous freezing yielded better agreement with observations. Fifth, model calculations of cirrus formation were greatly improved.

Field evidence about ice formation in cirrus and in wave clouds at temperatures near the homogeneous freezing temperatures of water was obtained both by direct sampling from aircraft (Sassen and Dodd, 1988; Heymsfield and Miloshevich, 1993, 1995; Jensen et al., 1994, Ström and Heitzenberg, 1994) and from lidar observations (Sassen and Dodd, 1988; Sassen, 1992). These papers are augmented by the growing body of publications reporting aircraft, lidar, radar and satellite observations of cirrus and other upper tropospheric clouds in general; these works continue to confirm that the great majority of these clouds is composed of ice crystals at concentrations of few tens to few hundreds per liter. While radiative properties of some cirrus indicate that higher numbers of small crystals may be present, this point is still not clarified. One of the direct observations of ice nucleation is the brief aircraft sounding reported by Sassen and

Dodd (1988); the transition from droplets to ice crystals was observed within a height interval of 50 m in slowly ascending air at a temperature between -35.0 and -35.6°C. These aircraft data were supported by a change in lidar depolarization ratio corresponding to the phase change. Heymsfield and Miloshevich (1993, 1995) report more detailed aircraft data that lead to very similar conclusions. Ice formation was observed to be sparse at temperatures higher than -35°C, and became very rapid at temperatures of -37°C and lower. Importantly, humidity and updraft measurements accompanied the particle observations. The maximum relative humidities reached - limited by the uptake of vapor by growing droplets or crystals - were found to diminish with temperatures decreasing from near -34°C to -56°C. Ice formation rates went from near-zero to very high values just past the points of maximum relative humidity, consistent with the onset of homogeneous nucleation as solution concentrations just decreased and droplet sizes increased sufficiently for the freezing rates to become significant. For the conditions of the observations, measurable or 'significant' rates were estimated as 0.01 cm^{-3} s^{-1}. Calculated relative humidity peaks, based on observed droplet sizes at the onset of freezing, on laboratory values for J_{sl} and on assumed compositions of sulfuric acid for the nuclei of condensation, showed good agreement with observations. The representativeness of sampling from aircraft, the inaccuracies involved in obtaining truly Lagrangian observations and the fact that all the data cited come from the same season and location (October-December, Colorado) are some of the limitations that have to be borne in mind.

Stimulating results from colder temperatures were reported by Knollenberg et al. (1993) and by Ström and Heitzenberg (1994). Both sets of observations, in the tops of tropical cumulonimbus at temperatures near -80°C and in orographically induced cirrus at -55°C, indicated the presence of small ice crystals (10..20 µm) in concentrations reaching 10^4 L^{-1}. These concentrations are much higher than those usually observed for particles which can be definitely identified as crystals by direct capture or by imaging probes. According to Knollenberg et al., the most likely source of these crystals was the freezing of sulfuric acid droplets near the

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cloud-top temperatures, though the origin of crystals at lower levels in the clouds couldn't be ruled out. When combined with the results of Arnott et al. (1994) it is clear that the sizes of cirrus particles, at least at temperatures below -40°C, tend to have a wide spread, tending to negative exponential distributions for sizes up to about 100 µm and more variable above that. Analyses of optical properties of cirrus have also pointed to the existence of large numbers of small crystals. It will be interesting to see to what extent the differences between these observations and those summarized in the preceding paragraph originate from different instrumental capabilities and from real variabilities in cloud properties.

New laboratory data on homogeneous freezing was produced by DeMott and Rogers (1990). Using a large chamber subjected to slow expansion, they obtained measurements of J_{sl} in the temperature range -30...-38°C. At temperatures above -34°C there was evidence for a significant contribution by heterogeneous nucleation. (The solute effect resulting from the CCN on which the cloud droplets form is negligible for droplet sizes of several µm diameter in the chamber.) The rates deduced by DeMott and Rogers compare well with the rate estimated by Sassen and Dodd from field data: J_{sl} ; 10^7 cm^{-3} s^{-1} at -36°C, however the magnitudes of the experimental uncertainties are not well known and can be expected to be quite large owing to the indirect way that nucleation rate is deduced. In fact, it is clear that neither cloud chamber experiments, nor experiments with droplets suspended in other media (emulsions) can be freed from quite fundamental limitations in the determination of J_{sl}.

The theory of homogeneous freezing has been reexamined in several of the papers already cited, and received a thorough revision by Pruppacher (1995). His formulation of the classical theory incorporates improved values for the thermodynamic constants, and incorporates singularities of these constants near -45°C (suggested by Angell (1982), and argued against by Bartell and Huang (1994)). However, the activation energy is estimated by Pruppacher from empirical values of J_{sl}, so that only consistency, not proof, has been achieved between theory and experiment.   The classical nucleation theory of spherical embryos with bulk

properties has been refined by the diffuse interface theory of Gránásy (1993) and applied to the homogeneous freezing of water (Gránásy, 1995); he reports substantially improved agreement with observations.

Observations of liquid droplets at temperatures lower than -40°C indicate some limit to generality of the role of homogeneous freezing in upper tropospheric clouds. Hallett and Lewis (1967) argued on the basis of optical phenomena, Sassen (1992) showed lidar depolarization data, and there are a number of reports of aircraft icing, all indicating that liquid droplets can exist in the atmosphere at temperatures below -40°C. These observations can be interpreted as evidence for the existence of haze particles at those conditions, below the saturation needed for growth to droplets. The associated question is what may be the freezing temperatures of such haze droplets? That question is even more acute with respect to the freezing of sulfuric acid aerosol and of sulfuric acid-nitric acid-water mixtures in the stratosphere. Observations in polar stratospheric clouds (PSC's) showed clearly that transformations to solids take place at temperatures below 195 K, but the conditions and chemical composition of the clouds are still subjects of intense investigation (e.g. Tolbert, 1994). Earlier attempts to determine the nucleation temperatures of H_2SO_4/H_2O solutions with relatively large sample sizes (Ohtake, 1993; Song, 1994) appear to have been influenced by heteronuclei, as evidenced by the small differences between the melting point curves (Gable et al., 1950) and the freezing points for acid concentrations to about 35% by weight. Beyer et al., (1994) working with smaller samples (5µl) found approximately 225 supercooling, still less than the accepted values for homogeneous nucleation. Recent data by Bertram et al. (1996), working with aerosol rather than bulk material, show much colder nucleation temperatures for this concentration range, falling along a smooth curve starting from the homogeneous nucleation temperature of about -35°C for pure water. This curve is very close to the theoretical estimates of Jensen et al. (1994) and of Larsen (1994) based on equations for homogeneous nucleation and on extrapolations of the relevant constants. The agreement between observations and theory (for the 0...35% concentration

range) is fairly reassuring, though some reservations must be expressed. First, the formation of an ice embryo in a surrounding of both H_2SO_4 and H_2O molecules in the liquid state should consider different kinetics than truly homogeneous nucleus formation. Second, solution effects for equilibrium conditions are used to estimate effects on homogeneous nucleation temperatures even though experiments such as Rasmussen and Mackenzie (1972) and Ganguly and Adiseshaiah (1992) showed that homogeneous nucleation temperatures are depressed by significantly larger amounts than the melting temperatures. The importance of this factor is emphasized by DeMott et al. (1994). Large uncertainties must therefore be acknowledged in the theory, even beyond the difficulty of assigning appropriate interfacial energy values. On the experimental side, the control of composition and of humidity, as well as the observation of the phase change are major difficulties. Further work on these topics is clearly warranted, including determinations of the chemical composition of the aerosol involved. While there is ample evidence for the prevalence of sulfuric acid aerosol in the upper troposphere, and the involvement of nitrates in the polar stratosphere, there are also disparate observations such as those of Hagen et al. (1995) and of Podzimek et al. (1995) of small fractions of soluble material in upper tropospheric aerosol in the size range 0.04...0.13 µm, and the existence of larger particles (to 5 µm diameter) in concentrations of the order 1 cm^{-3}. It is worth noting that the formulation of detailed models of cirrus and PSC formation (Jensen et al., 1994; Larsen, 1994; Heymsfield and Miloshevich, 1995) and the parametric model of DeMott et al. (1994) offer the opportunity to evaluate theoretical and laboratory results in comparison with field data.

For acid concentrations between 35% and 67% by weight, the solid phase is assumed to be sulfuric acid tetrahydrate (SAT). The large-volume experiments of Ohtake (1993) and of Song (1994) yielded solidification temperatures near 200 K, but with a large degree of scatter. Beyer et al. (1994) report similar temperatures but also show that the length of time to solidification is quite large, so that the freezing of small sulfuric acid aerosols of high concentrations is unlikely. Anthony et al. (1995) report on the basis of FTIR observations that

submicron sulfate aerosol of 35...90% composition remained liquid for periods up to 3 hours when held at temperatures between 190 K and 230K. It thus appears that homogeneous nucleation in such sulfuric acid aerosol will only take place at temperatures < 190 K. For practical applications to PSC's, ternary systems involving water, sulfuric acid and nitric acid need to be considered but will not be discussed here as they are covered by the review paper of T. Peter in this volume.

3. Clouds in the lower troposphere

The formation of ice in lower tropospheric clouds, between the temperatures of the melting point and of homogeneous nucleation, remains a question of great importance for understanding the global climate and water balance yet progress is quite slow in this area. The fundamental problem is that the origins of ice particles are understood only partially and in very rough terms. Predictive capabilities are limited by the complexities of tropospheric aerosol, by inadequate theoretical formulations and by the lack of proven instrumentation for ice nucleus measurements. Interpretations of field observations are hindered by the direct connections between ice formation and cloud dynamics and by the existence of secondary ice generation processes. Recognition of these limitations resulted from the period around the 1970's which saw intense laboratory experimentation as well as numerous field studies utilizing aircraft equipped with ice particle probes. The major findings of that period, and progress since then, led to the recognition that ice particle concentrations in clouds are at times much higher than measured ice nucleus concentrations, that some of that discrepancy is due to secondary processes such as the Hallett-Mossop process, and that ice nucleation can proceed via different pathways and from a variety of natural nucleating substances. The current situation can be best characterized as one focussed on searching for solutions to overcome or bypass one or other of problems which stand in the way of making the findings more precise, more specific to given cloud systems and instances. Inherent to this search is the openness to new ideas.

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Two concepts have been put forward that may lead to new findings. Braham (1986) and Beard (1992) call attention to the fact that in warm-based convective clouds the freezing of rain or drizzle drops grown by coalescence seems to be a key element of ice initiation and development. Field observations of Rangno and Hobbs (1991) in maritime clouds appear to support the role of drop freezing in what they term the first stage of ice enhancement. In contrast, for continental clouds Rangno and Hobbs (1994) show evidence for possible linkages between cloud depth and the width of the droplet spectrum at cloud top and ice initiation. Common to all of these scenarios is some connection between events traditionally considered part of the warm-rain process and ice development. Possible mechanisms that lead to preferential freezing of the larger cloud droplets or rain drops are condensation on large condensation-freezing nuclei or the capture of large freezing nuclei by the drops. These processes have not yet been properly observed. Also, the relative sparsity in precipitation samples of freezing nuclei active at temperatures above -8°C would have to be reconciled with the idea of drop freezing in clouds by demonstrating that the activity is lost with time.

The other suggestion that is motivating further investigations is that the residues of evaporating cloud droplets have enhanced ice nucleating abilities. Beard (1992) explores this idea and also links it with the possibility that such residues might be the contact-freezing nuclei discussed in the preceding paragraph. Laboratory evidence for this process is claimed by Rosinski and Morgan (1991).

The measurement of ice nuclei with high spatial and temporal resolution as well as with indication of the mode of action remains an elusive goal. Some progress may emerge from the continuous-flow diffusion chamber design of Rogers (1994). In laboratory studies of silver iodide and related aerosols, DeMott (1995) showed the that the relative contributions of different nucleation modes depend on the aerosol type, temperature and, in some cases, on the specific history of when the aerosol is introduced into the cloud. These data opened the opportunity for

more detailed comparisons with the results of cloud seeding (Meyer et al., 1995) than has been possible earlier. In general, modeling of the initiation of ice is done in ever greater detail, though the input assumptions remain roughly defined (e.g. Meyer et al., 1992). On the other hand, Baker (1991) performed calculations to show that a process often considered in ice nucleation - activation by high supersaturations with respect to water - is unlikely to be significant in clouds.

4. Organic ice nuclei

While monitoring of atmospheric ice nuclei, and observations of their activity in creating ice particles within clouds, are the principal concerns for establishing the origins of ice in clouds, the questions what substances and what mechanisms make efficient heteronuclei are clearly complementary to the primary foci. Important new results in these areas are summarized in the following paragraphs.

Epitaxial fit between ice and the nucleating substrate is a well known factor favoring nucleation. That an alcohol *monolayer* could provide such a substrate and nucleate ice at temperatures near -1°C was a startling discovery (Gavish et al., 1990). In fact many details of the monolayer structure, of the monolayer-ice interface and of the size of the ice embryo has now been elucidated by Popovitz-Biro et al. (1994) and Majewski et al. (1994).

The initial work reported in 1990 demonstrated that 2D crystals of aliphatic alcohol monolayers whose lattice dimensions are close to that of ice would be efficient ice nuclei. The alcohol series $C_nH_{2n+1}OH$ for n=16...31, in the form of monolayers spread over water drops, produced a double series of nucleation temperatures for as n increased. For each series, nucleation temperatures rise toward higher values from near -14°C, the freezing temperature found for the smallest n-values. For even values of n the highest nucleation temperatures reached -8°C for n>22, and for odd values of n the nucleation temperatures gradually rose to near -1°C for n=31. In comparison, carboxylic acids of similar chain lengths produced ice nucleation at temperatures around -16°C. The lattice match, as determined by grazing-incidence

X-ray diffraction (GID), was better for the alcohols than for the acids confirming the role of epitaxy.

In the more recent reports, measurements with D_2O covered with the aliphatic alcohol monolayers confirmed the findings with H_2O, showing the same series of nucleation temperatures but shifted toward higher temperatures. Monolayers of mixtures of two different alcohols, which produce poorly ordered surfaces, led to lower nucleation temperatures than either of the components separately; this confirms the role of structural fit to ice. This contrasts with the situation when up to 50% of a fluorocarbon alcohol is mixed with the n=20 hydrocarbon alcohol: no change in nucleation temperatures was found indicating that these two alcohols form separate crystalline domains. The influence of the chain length is interpreted as governing the lateral coherence length, and the tilt angle of the chain with respect to the b-axis, in all leading to better lattice match with increasing chain length. Perhaps the most difficult point to clarify is the reason for the difference between the even and odd members of the series, for example why the two longest members of the series, n=30 and n=31 yield nucleation temperatures differing by 7°C. There is no clear evidence for differences in packing arrangements, so the hypothesis is that the orientation of the (CH_2OH) head groups, and possibly rearrangement of this group, account for the differences in nucleating ability. This notion is also supported by experiments with alcohols in which ester or amide groups have been inserted mid-chain; the dependence of nucleation temperatures on overall chain length and parity was overridden by a dependence of the parity of the hydrocarbon fragment connecting the OH head group to the introduced functional group.

Examinations, using GID, of the monolayers just prior to and immediately following ice nucleation, as well as GID patterns from the ice itself allowed Majewski et al. (1994) to set an upper threshold for the critical size of the ice embryos at temperatures very near 0°C. A coherence length of 25 Å was found for ice formed under the alcohol monolayer (which in itself has much larger coherence length) so that the critical size of nuclei is taken to be about 20 Å corresponding to about 50 water molecules. [This is a surprisingly small critical size, comparable

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to that estimated to be necessary for homogeneous nucleation near -40°C.] In addition to the critical-size estimates, the GID observations showed that the monolayer undergoes a gradual change as the temperature is lowered from 6°C to 1°C but retains its structure through nucleation, growth and subsequent melting of the ice underneath it. The nucleated ice crystals were shown to have their c-axes perpendicular to the interface. Since binding of an ice layer to the monolayer would impose proton ordering, the question arises, and remains unanswered at this point, how far this proton ordering might extend into the ice.

At least a partial, independent confirmation of the nucleating abilities of the aliphatic alcohol monolayers is given by Davey et al. (1994). Working with the relatively inactive n=30 member of the series, they found that nucleation with that monolayer is almost immediate at -8°C, and that at higher temperatures, to -4°C, nucleation will take place with gradually increasing delay times (to near 12 h at -4°C). Unfortunately, the nucleation temperatures observed with the monolayer in their apparatus differed only by few degrees from those obtained in the control experiments, so that the presence of other sources of nucleation can't be ruled out.

The difference noted many years ago between threshold temperatures for freezing nucleation of chiral or racemic varieties of amino acids was confirmed anew by Gavish et al. (1992). These materials have very poor lattice fit to ice and do not differ in this respect from one another. Thus the observations require other interpretation. By noting that higher nucleation temperatures are found for those varieties that have polar axes, independently whether that occurs for the chiral-resolved or racemic variety, the authors propose that electric fields within cracks of the crystals raise the nucleation temperatures. Visual observations confirmed that cracks are preferred locations for deposition nucleation at -15°C. Macroscopic electric fields, and electric charges on particles have been suggested before as factors in ice nucleation, but solid evidence has been difficult to produce; whether the suggestion for this microscopic electric-field effect will be more amenable to confirmation will remain to be seen.

Bacterial ice nuclei were discovered in the 1970's. Their activity as freezing nuclei at temperatures as high as -2°C raised a great deal of interest in identifying the active agents. Practical applications were identified for bacterial nucleants as initiators of freezing, as well as for the elimination of these bacteria and consequent delaying or elimination of freezing in natural systems. Fungal species of similar activity were also found by the late 1980's. Most of the material relating these biological ice nucleants is now assembled in a single volume (Lee, Warren and Gusta, 1995) so readers are referred to that for details. What is missing from the compendium, for lack of any systematic attack of the issue, is work on the possible atmospheric role of these nucleants.

For evolutionary reasons still not known, bacteria of a handful of species (out of the millions in existence) developed the ability to synthesize ice nucleating proteins in their outer membrane. In contact with supercooled water they initiate freezing at temperatures close to 0°C. The fraction of individuals within a population of bacteria (either natural or cultured) which nucleate ice at a given temperature is quite variable and often quite small. Also, the nucleating material is a small fraction of the bacterial membrane. These facts made identification and isolation of the active agent quite difficult. It was accomplished by identifying the DNA segment responsible for expression of nucleating ability, confirming this by splicing this gene into otherwise non-active species and then deducing the protein structure that the gene elicits. Presence of the protein in the outer membrane was confirmed and visualized by antibody attachment; the protein forms clusters of a large range of sizes in abundances related to the activity of the sample. The protein molecules are 150...200 kDa size and are characterized by repetitive segments of nucleotides. Quantitative comparisons between protein amount per cell, numbers of clusters and nucleating ability led to the realization that activity is a function not only of the amount of protein produced but also of factors governing its aggregation. What these factors are is not yet established, nor is the structure of the nucleating site. Gamma ray deactivation analysis led to an estimation of the sizes of the nucleating units: at -13°C a single

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protein molecule may be sufficient while at -3°C a cluster of . 10^4 molecules is indicated.

Perhaps the broadest impact that studies of organic ice nuclei have is that they produced new, quantitative methods for the characterization of the nucleation process and of the substrate surface. At the same time, ice nucleation came to the attention of scientists in diverse fields of research, with many of these scientists using ice nucleation as an analytical tool for the elucidation of genetic, plant pathological and many other problems. Implications for atmospheric ice nucleation are speculative - there is little known about the organic components of atmospheric aerosol in general, and it seems certain that research to improve that situation will be quite demanding considering the tiny amounts of organic material that may be involved in producing ice nucleation. Assessments of particles of biological origin in air and in precipitation (e.g. Matthias-Maser and Jaenicke, 1992; Casareto et al., 1996) indicate that the search should be continued.

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