ICE NUCLEATION — THEORY

A TUTORIAL

FOR PRESENTATION AT THE NCAR/ASP 1999 SUMMER COLLOQUIUM

Gabor Vali
<vali@uwyo.edu>; http://www-das.uwyo.edu/~vali

The homogeneous and heterogeneous nucleation of ice are described in terms of the 'classical' thermodynamic/kinetic theory, and in terms of various qualitative notions suggested by empirical results. The aim of this presentation is to provide a general, intuitive and critical appreciation of the issues involved. It is not meant to be exhaustive or definitive. Focus is on ice nucleation in the atmosphere.

June 25, 1999
(with corrections October 17, 1999)

1. General concept of nucleation.

The creation of a new phase from a metastable (supersaturated or supercooled) state occurs via *germs*, or embryos, of the new phase. Germs are small, transient clusters of the new phase, or something approximating it, which exist in various sizes, dispersed within the parent phase. Continuous fluctuations in the sizes of these clusters, via the incorporation of additional molecules and the detachment of others, may result in a germ growing large enough to become stable, i.e. for growth to become overwhelmingly more probable than decay. This is expressed as reaching the *critical size* for stability, and hence nucleation of the new phase. The instability of germs smaller than the critical size and the stability of those larger than the critical size arise from the decreasing surface to volume ratio of the germ with increasing size. Molecules at the germ's surface are most likely to return from the germ to the metastable phase, so that the higher is the proportion of interior molecules the more likely it is that the germ will become permanent and grow.

In addition to the above picture, in which germs are viewed as isolated clusters dispersed in the parent phase, the situation needs to be considered in which the germs are attached to some pre-existing structure, most likely a solid surface, in such a way that the likelihood for the germ to reach stability is increased. This is the *heterogeneous* nucleation case, compared to the previously considered *homogeneous* case. Be definition, homogeneous nucleation requires a greater degree of metastability - supercooling or supersaturation - than heterogeneous nucleation.

Ice formation from the vapor phase is termed *deposition*, while ice nucleation from the liquid is termed *freezing*.

In the atmosphere, ice nucleation may be either heterogeneous or homogeneous freezing, or heterogeneous deposition. Homogeneous deposition does not occur in the atmosphere. This conclusion can be drawn by comparing atmospheric conditions with laboratory evidence and theory for the requirements for the various nucleation pathways.

2. Theoretical formulations.

The major questions associated with the description of nucleation given in the preceding paragraphs are:

- How to characterize the strength of the bonding between molecules within the germs? Do they have the same properties as the bulk phase that is to be nucleated?
- How are molecules at the outer surface of the germ bonded? What is the interaction of a molecule at the surface of the germ with those in the parent phase nearby.
- How to characterize the interaction of molecules within the germ with the substrate surface in the case of heterogeneous nucleation?
- Are molecules added to the germ from the parent phase singly, or at times in doublets, or in cascades?

Clearly, these are difficult issues that are intimately related to the bulk properties of the parent phase in its metastable condition, to the bulk properties of the new phase (ice), and to the possibly intermediate properties of the germs, plus to the kinetics of the interchange of molecules between the germ and the parent phase. It is evident that full treatments of these questions are neither within the reach of theoretical treatments, nor of direct experimentation. The two major theoretical approaches developed to date are the thermodynamic/kinetic approximation and molecular simulations. While the latter is fundamentally more attractive, that approach has not yet developed to the stage of providing significant new insights or usable predictions. On the other hand, the thermodynamic/kinetic treatment has a century of development behind it. The basic ideas of this approach have changed little since the earliest times, but marginal gains are still forthcoming, at least in the description of homogeneous nucleation. The thermodynamic/kinetic theories of heterogeneous ice nucleation may be viewed as useful guides and syntheses but are limited by the difficulties that attach to many of the integrative quantities it relies on, and have few rigorously tested results.

3. Thermodynamic/kinetic theory

3.1 Homogeneous ice nucleation

In terms of thermodynamic potentials, or free energies, the new phase has a lower bulk energy. That is why it is the stable phase at the conditions considered. The volume energy of the germ is thus negative, and proportional to the number of molecules in the germ. The surface energy between the germ and the metastable (parent) phase is positive and is roughly proportional to the 2/3 power of the number of molecules. The sum of these two terms has a maximum at the critical germ size, indicating that below that size growth is energetically not favored, but beyond that size growth is spontaneous as increasing size leads to decreasing total potential for the cluster.

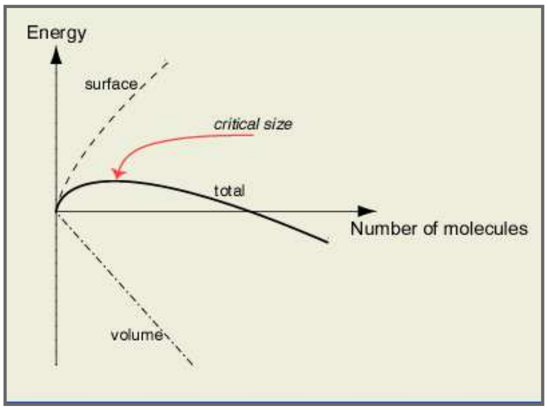


Fig. 1. The free energy of a germ of the new phase as a function of the number of molecules in the cluster.

Clearly, the limit to the situation depicted in Fig. 1 is reached when there is no more of the parent phase left so that the surface energy term suddenly goes to zero and the total energy becomes the bulk energy of the new phase. More precisely, the energy depicted in the figure is the change in free energy from that in the metastable phase, ΔG, and therefore the final energy state is lower than the initial one.

The next question to consider, in this broadbrush description, is how to describe the fluctuations in the size of the germs, given that the free energy function is as depicted above. The approach here is to assume that the steady-state distribution of germ sizes up to and including the critical size is given by a Boltzmann distribution corresponding to the energy change $\Delta G(n)$ for n molecules in the germ:

$$N(n) = N_o\, e^{-\Delta G(n)/kT}$$

where $N(n)$ and N_o stand for the number of germs and the number of single molecules per unit volume of the parent phase. [Application of the Boltzmann distribution here is connected with Einstein's theory that the probability of some state arising by fluctuation is proportional to the negative exponential of the entropy change involved.] An estimate of the flux of germs growing past the critical size n^* is made as the number of germs with size (n^* - 1) times the net rate of impingement of molecules on a surface corresponding to a sphere of n^* molecules. This product is termed the nucleation rate, J. The units of J are [$L^{-3}\ T^{-1}$]. This leads to equations of the form

$$J = A\ e^{-\Delta G^*/kT}$$

where ΔG^* is the free energy change associated with the formation of germs of critical size. The pre-exponential factor, A, depends on slowly varying quantities such as the concentration of molecules in the parent phase, molecular mass, temperature and others; it can be taken as a constant for purposes of examining the main factors influencing the nucleation rate. The main dependence of the nucleation rate on supersaturation or on supercooling is through ΔG^*.

The foregoing treatment skipped many details. These involve, principally, attempts to account for the difference between the non-equilibrium situation of embryos growing to super-critical size and the stable condition for which the equations strictly speaking apply. [In the stable case, that is below saturation and above the melting point, $\Delta G(n)$ increases monotonically with n, so the probability for growth of a molecular cluster never exceeds the probability of its decay.] The estimation of material constants such as heat capacity, latent heat, and others, for the metastable state and for very small entities of the new phase are other difficulties that have to be addressed. Further refinement involve different ways of answering the three questions listed (with bullets) above. Some of these will be presented in later sections.

Fuller derivations of the nucleation rate expression can be found in large numbers of texts. Götz, Mészáros and Vali (1991), Young (1993) and Pruppacher and Klett (1998), among others, present detailed treatments.

The specific form of J for deposition (vapor to solid) nucleation can be given as:

$$J = A\ exp\left[-\ B\ \frac{\sigma^3}{T^3}\ \frac{1}{(\ln S)^2} \right]$$

where A and B are constants (approximately), σ is the interfacial energy between liquid and vapor, T is absolute temperature, and S is the saturation ratio. This equation has been well accepted now for many years and there are only small differences among authors in the evaluation of the constants. The equation is also valid for homogeneous nucleation of the liquid phase from the vapor (condensation).

The expression for freezing is more controversial because of alternative ways of estimating the free energy change using temperature and pressure-dependent density, specific heat, etc. The form given below is from Jeffery and Austin (1998), and will be discussed in more detail later:

$$J = A_{\mathrm{f}}\ \sigma_{\mathrm{i/w}}^{1/2}\ exp\left[-\ B_{\mathrm{f}}\ \frac{\sigma_{\mathrm{i/w}}^3}{kT}\ \frac{1}{\{\ln[T_{\mathrm{m}}/T]\}^2} \right]$$

with A_f and B_f denoting quantities which also depend on temperature but are given here in this simple form to demonstrate the most important temperature dependence of J; $\sigma_{i/w}$ is the interfacial tension between the liquid and ice, T is temperature and T_m is the melting point (273 K). The part of A_f that expresses the flux of molecules to the embryo is in this case estimated as an $e^{-\Delta g/kT}$ term with Δg called the 'activation energy'. This quantity is determined from self-diffusivity measurements.

Both of the above equations show that the nucleation rates are highly sensitive to the interfacial tension. This leads to a serious limitation in the use if these equations, as the interfacial tensions are virtually unmeasurable at the conditions at which the nucleation rates are to be calculated.

The two equations also indicate that J can change very rapidly with S or with T. Those very rapid changes give rise to the concepts of threshold supersaturation and threshold temperature, usually defined as S_{th} or T_{th} corresponding to $J = 1\ \mathrm{cm}^{-3}\ \mathrm{s}^{-1}$. The sharp onset of homogeneous nucleation is in accord with observations, and takes place, for ice, near $S_{th} \approx 5$–8, and $T_{th} \approx -40$°C. Homogeneous deposition is not possible in the atmosphere, first, because of the high supersaturation that is required, second, even if that were not the case, in accordance with Ostwald's rule of stages, at temperatures below the melting point, the liquid phase forms first and freezes rather than the direct vapor-to-solid phase transition. Homogeneous deposition was included in this discussion only to show the formulation and as preparation for dealing with heterogeneous deposition.

The nucleation rate for freezing calculated by Jeffery and Austin (1997) is shown in Fig. 2 along with some experimental results. The observations shown, except the two points at the lowest temperature, were obtained in laboratory experiments with small droplets. The droplets were either produced as clouds or were dispersed in oils. Nucleation rates in the experiments are evaluated from the fraction of drops frozen at given temperatures, their volumes, and the assumption that the freezing of a droplet is due to a single critical germ forming within it.

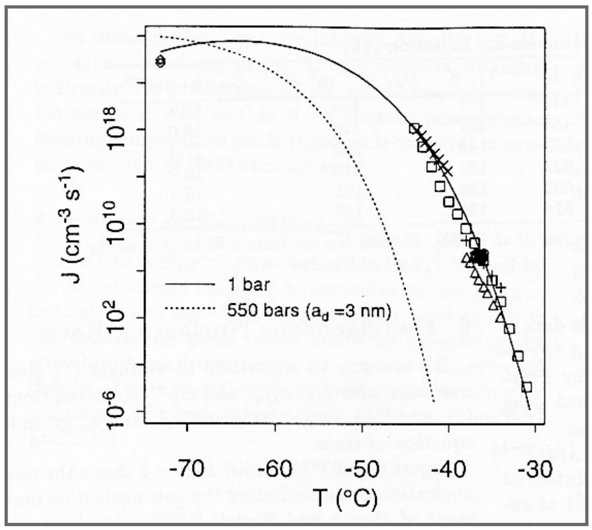


Fig. 2 (from Jeffery and Austin, 1997). The calculated nucleation rates are shown as lines for two pressures. Observations are from: o – Wood and Walton (1970); Δ – Butorin and Skripov (1972); + – DeMott and Rogers (1990); × – Hagen et al. (1981), and ◇ – Huang and Bartlett (1995). These points at -72°C are from observations with droplets of about 3 nm radius and internal pressure of 550 bars. Points indicated by are calculated values from Pruppacher (1995).

The agreement shown in Fig. 2. between observations and theory is quite reassuring. The Jeffery and Austin results were obtained from a revised equation of state for the density and entropy of liquid water. The interfacial energy $\sigma_{i/w}$ was obtained via an empirical relationship to the latent heat of melting, which in turn was predicted from the equation of state. The activation energy, Δg, was estimated from self-diffusivity measurements fitted with an empirical expression. In this way, the Jeffery and Austin results can be viewed as a combination of theory with measurements of fundamental properties of water. The results are further supported by its apparently correct predictions for the pressure-dependence of nucleation temperatures (not shown here in detail). For temperatures >-45°C, theoretical estimates have been fairly stable for many years and the Jeffery and Austin results are not much different from earlier estimates. For temperatures <-45°C, there is only the one set of observations, by Huang and Bartell, and this too shows agreement with the theory. These results contradict Pruppacher's (1995) conclusion that, on the basis of indications for a singularity in the behavior of water at -45°C, the nucleation rate would also have a discontinuity at that temperature.

In more practical terms, the experimental results can be shown as freezing temperatures of droplets of various sizes. A set of such results is shown in Fig. 3.

The freezing temperatures shown in Fig. 3 represent somewhat different measures from experiment to experiment. In some cases it is the average of the observed temperatures for individual droplets of given size, in others it is the temperature at which 90% of the droplets were froze, and so on. Variations also exist in the rate of cooling of the samples, and that too influences the freezing that results from some nucleation rate. However, it can be shown that the relationship between the nucleation rate, J, and the fraction of drops, $N(T)/N_0$, predicted to be unfrozen at temperature T can be expressed as

$$\int_{T}^{T_m} J(T)\,dT = \kappa \frac{\gamma}{V} \quad \text{with} \quad \kappa = -\ln[N(T)/N_0]$$

where γ is the rate of cooling (sec^{-1}) and V is the volume of the droplets. The constant $\kappa = 0.693$ for the median (50% unfrozen), $\kappa = 2.3$ for 10% remaining unfrozen, etc. Coupled with the rapid variation of J with T (Fig. 2) it can be seen that the variations in cooling rate and in the fraction of drops actually represented by the data points in individual cases will influence the reported T-values to rather small extent. In this way, one can also demonstrate that the data shown in Fig. 3 are consistent with the rate curve in Fig. 2. In fact, some of the points in the two graphs are from the same experiments.

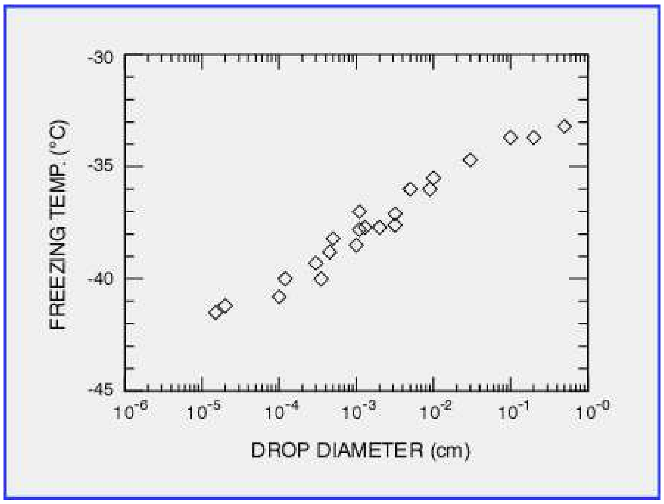


Fig. 3. Observed freezing temperatures for drops of pure water from a large variety of different experiments.

3.2 HOMOGENEOUS ICE NUCLEATION IN HAZE PARTICLES

Special consideration needs to be given to the case where freezing nucleation takes place in solution droplets. The main reason for this is evidence from cirrus studies that ice formation is initiated at humidities below saturation with respect to water. The most plausible interpretation of this is the freezing of water in deliquesced soluble materials, i.e. haze particles.

The effects of solutes on homogeneous ice nucleation consist of two parts. First, the equilibrium melting point of the solution is depressed, and, second, all the factors influencing germ formation are altered to some degree. Since melting does take place without passing through a metastable state (no superheating), knowledge of the equilibrium melting point is sufficient. The magnitude of the melting point depression is reasonably well known at least for ionic solutes. At relatively low (up to few molal) concentrations, the change in melting temperature is proportional to the concentration of ions in the solution, giving roughly 1.9°C change per mole of ions. Deviations from this rule, and melting point depressions for high solute concentrations are best determined experimentally. High solute concentrations at the beginning of haze particle growth often coincides with temperatures where homogeneous ice nucleation is expected in the upper troposphere and in the stratosphere.

According to the rather sparse set of empirical results, homogeneous freezing temperatures are depressed by solutes to an even greater extent than the lowering of the melting point, so that

$$\Delta T_{\text{soln}}^{\text{hom}} = \lambda \cdot \Delta T_{\text{soln}}^{\text{melt}}$$

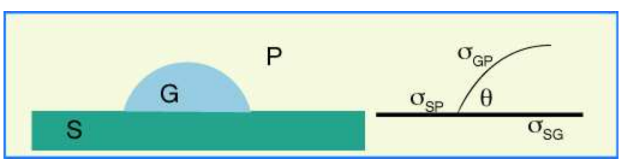
where the factor λ has values between 1 and 2. Most data appear to be clustering around $\lambda = 1.7$. The larger than unity value for λ is certainly a reflection of the fact that the solute alters the conditions for germ formation, and that is not at all surprising, but the mechanism responsible for this result is unknown in detail.

In recent calculations of the nucleation rate in solution droplets, Tabazadeh et al. (1997) accounted for solution effects in essentially the same way as given here. They estimated the ice/solution interfacial energy as the difference of ice/vapor and solution/vapor interfacial energies (Antonoff's rule) and worked backwards from measured nucleation temperatures to derive the best values for the activation energy Δg. The Δg -values so obtained differed significantly from values derived from viscosity data, specially at temperatures below 205 K. Overall, while this procedure led to a usable rate equation, it is clearly not on very solid grounds. There is considerable room here for future work, and the importance of understanding cirrus formation puts emphasis on the need for better results.

3.3 HETEROGENEOUS NUCLEATION

While theory and experiments can at least be reconciled for homogeneous ice nucleation, theoretical treatments of nucleation on foreign surfaces are very difficult to relate to observations. A large part of the problem, in addition to the general questions already listed, comes from the difficulty of characterizing surfaces, and the specific features on them that serve as catalysts for ice nucleation. Needless to say, many attempts have been made to deal with the problems, and there is a rich body of literature to attest to this. Even so, it is fair to say that the theory serves more as a synthesis of ideas and a frame of reference for further studies than a basis for quantitative results on heterogeneous ice nucleation.

The simplest and most fundamental notion for viewing heterogeneous nucleation derives from the phenomenon of wettability and its reflection in the contact angle. On an insoluble substrate (S), the germ of the new phase (G) is assumed to have a spherical cap shape with the contact angle characterizing the relationship between the three interfacial energies involved. This is illustrated below:



$$m \equiv \cos\theta = \frac{\sigma_{SP} - \sigma_{SG}}{\sigma_{GP}}$$

This expression for *m* follows from the requirement of equilibrium at the edge where the liquid meets the solid. A small contact angle ($m \approx 1$) means wettability. At the other limit of $m = -1$ the liquid would be a sphere sitting on top of the solid; this is the ideal non-wettable solid. While this model is based on the formation of a liquid germ from the vapor, more precisely it states the requirement for equilibrium between a liquid droplet on a surface and the surrounding vapor, it is also adopted as the basis for heterogeneous nucleation of solids from a liquid parent phase (P).

In the simplest formulation of nucleation in terms of spherical germ shapes, the critical germ size depends only on the radius of the germ and it can be shown that this critical radius is also a sufficient criterion for nucleation with a germ of spherical cap shape (as illustrated above). The free energy of formation of the spherical cap germ is reduced in comparison with that of a full sphere of the same radius, principally because of the smaller surface area between the parent phase (P) and the germ (G). Secondarily, the interfacial energy of the germ with respect to the substrate (S) is lower than with respect to the parent phase; the degree to which this is true determines the 'efficacy' of the substrate to serve as a 'good' heteronucleus. This latter point can be seen by recognizing that m=1 can arise from $\sigma_{SG} = 0$ and $\sigma_{GP} = \sigma_{SP}$. Pursuing this line of analysis, it is found that the free energy barrier to nucleation for a spherical cap can be written as the energy barrier for homogeneous nucleation times a factor *f(m):*

$$\Delta G^{het} = f(m) \cdot \Delta G^{hom}$$

where, for the geometry depicted above, $f(m) = (2+m)(1-m)^2/4$, which is a monotonic function varying between $f(m) = 1$ for $m = -1$ and $f(m) = 0$ for $m = 1$. Expressions for J show that even a modest values like $f(m) = 0.1$ corresponds to large changes in $S(J)$ or $T(J)$: for a given nucleation rate S changes from 5 to 1.3 and T from 233 K to 268 K.

In addition to the free-energy term, the changed geometry also modifies the pre-exponential term, but the result, as before, is relatively insensitive to this. Importantly though, the nucleation rate for heterogeneous nucleation must be expressed per unit surface area of the substrate in contact with the parent phase (vapor or liquid).

Starting from this general picture, the nucleation rate of ice on a substrate can also be deduced. The main factor to introduce is the appropriate form of *f(m).* A fairly evident step beyond the model with a plane solid substrate is to consider spherical solid surfaces; this model describes nucleation on aerosol particles. These results are shown in Fig. 4.

Another direction of elaboration is to consider germ shapes other than spherical, such as flat cylinders. For crystalline germs this is clearly desirable to do, and it is certainly a generally valid goal to estimate some optimum shape for the germs. A number of possibilities are shown in Fig. 5; several of these have been incorporated into calculations. In some cases the geometric shape is restricted not to include dimensions smaller than single layers of ice. On the whole, including different geometric configurations for the shape of the germ led to little additional power of the derived results. However, it must also be realized that germs may in fact be so small that descriptions in terms of simple geometric forms may be not be justified at all.

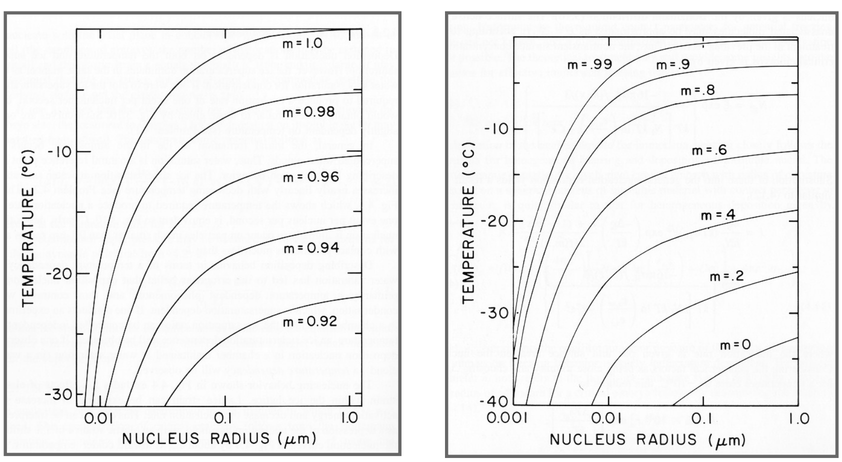


Fig. 4. Nucleation temperatures corresponding to $J = 1$ cm^{-3} s^{-1}, for deposition (left) and for freezing (right) on surfaces of indicated radii and for various *m*-values. (from Young, 1993)

The most difficult parameter to evaluate in this formulation is the interfacial energy between the germ and the substrate. There are no macroscopic values to use. Also, the interfacial energy may well depend on the curvature of the contact surface. The germ itself may introduce a strain in the underlying surface, changing the interfacial energy. Most importantly, there is ample evidence to show (see Section 6) that nucleation takes place on specific locations (sites) on the substrate surfaces, which is a clear indication of the dominant roles of specific surface features such as steps or dislocations. There is very little theoretical guidance on how to formulate descriptions of the interaction energy between such sites and the germs of ice.

In view of the difficulties just listed it is not surprising that the thermodynamic/kinetic theory of heterogeneous ice formation does not lead to useable quantitative predictions. This doesn't mean that there are no agreements between theory and observation; in fact quite a number of empirical results have been shown to be consisted with the theory. This was also the case for homogeneous nucleation. Yet, none of the experimental results could be called definitive tests or proofs of the theory, or of some part of it. So, confidence in the power of this theory is low. Also, there are a number of quite basic objections that can be raised about its validity. Overall, the main role of this theory is to suggest a general framework for thinking about the factors involved in heterogeneous nucleation.

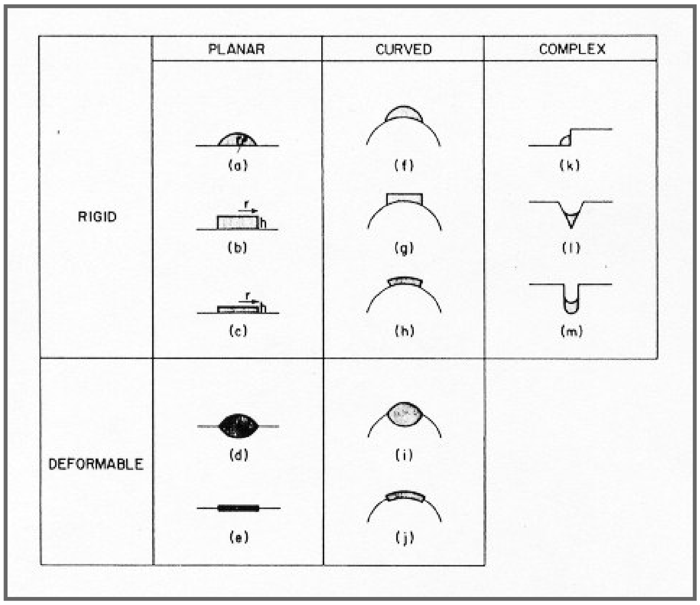


Fig. 5. Some simple shapes of ice germs on solid or deformable substrates.   (From Knight, 1979)

4. Modes of atmospheric ice nucleation.

As stated in Section 2, theory and observation agree in that homogeneous freezing of water droplets and of haze particles are processes that can take place in the atmosphere, and that homogeneous deposition is not to be expected. The answer to the question what heterogeneous processes are expected to be of atmospheric relevance, is both less certain and more complex. First, while deposition nucleation is theoretically possible and there is evidence from laboratory work that it does occur under given conditions, empirical evidence from atmospheric measurements is ambiguous. Second, several variants of the freezing process are of atmospheric relevance. Thus, several '*nucleation modes*' are recognized; these represent the different pathways in which some aerosol of potential nucleating ability, plus water vapor or a droplet, reach the point at which ice is initiated by the particle. Figure 6 shows some of these modes. There are good reasons to believe that these modes are not just abstractions but in fact have relevance to the atmosphere, although definitive proof is not yet available. It is generally assumed that the activation temperatures for the different modes are not the same, i.e. that $T_{act}^{i} \neq T_{act}^{d} \neq T_{act}^{t}$ where the superscripts refer to immersion freezing, condensation freezing and contact freezing, respectively. Furthermore, it is often assumed, with some experimental support, that $T^i_{act} < T^t_{act}$ i.e. that for the same particle contact nucleation activity requires less supercooling than immersion freezing. Less is known about other possible comparisons.

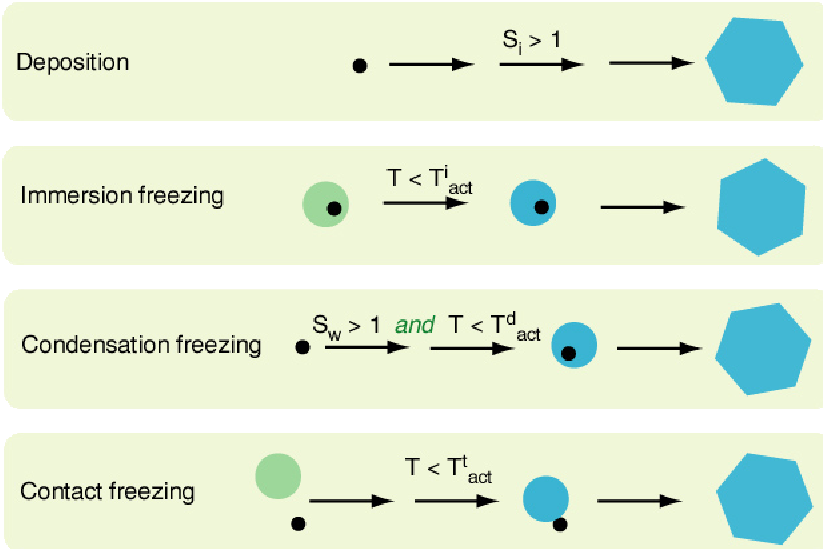


Fig.6. Schematic depiction of nucleation modes of ice in the atmosphere.

It is possible to write down expressions for the nucleation rate for each of the modes depicted in Fig. 5. For deposition and immersion-freezing these are the equations already cited. For condensation-freezing, one can combine the probabilities of condensation and that of freezing, while for contact-freezing the probability of collision between aerosol and water droplet has to be combined with the probability of freezing. If the assumption is made that the probability of freezing (nucleation rate per unit surface area, *J*, times the total surface of a particle) is the same for all freezing modes the expressions are relatively straightforward to construct. Of course, the real issue is how the nucleation rates for freezing via the different modes might in fact vary.

An interesting link between deposition and contact-freezing was suggested by Cooper (1974). He proposed that embryos of subcritical size with respect to deposition may be large enough to initiate freezing (have super-critical sizes with respect to freezing) when coming into contact with a supercooled drop. This led to a prediction of contact-freezing temperatures about half as far below 0°C as for deposition.

Another analysis of the relative roles of deposition and of freezing was given by Manton (1983) in which the thresholds for the two processes are examined and their dependencies on the contact parameter, *m*, are derived. Using reasonable values for the adjustable constants He showed fair agreement between theory, , and the laboratory measurements of Schaller and Fukuta (1979). Based on these results, the domains of the two processes are shown in Fig. 7.

The deduction that may be drawn from Fig. 7 is that deposition nucleation is of possible atmospheric relevance at temperatures of <-10°C or so. There are as yet no unambiguous tests from the atmosphere for this, or for Cooper's conclusions.

Let's make brief mention here of one of the consequences of the existence of various modes of ice nucleation. This is, that measurements of atmospheric ice nucleus concentrations have to be designed to either respond to some specific nucleation mode, or have to simulate the likely contributions of the different modes for given cloud conditions. If the first course is followed, separate measurements for each mode may be required, and in summing the results for given cloud conditions the assumption has to be made that there is no overlap among the populations of particles which respond to the various modes. If it were known that one or other mode would predominate in some given situation, then the measurement of that mode would be the obvious decision, but there is no evidence for this to be actually the case under atmospheric conditions. If the simulation approach is followed, then the questions arise to what extent the test cloud in an instrument represents conditions (supersaturation, droplet spectra, etc.) expected in clouds, and how to cover the range of conditions that may arise in clouds of different types.

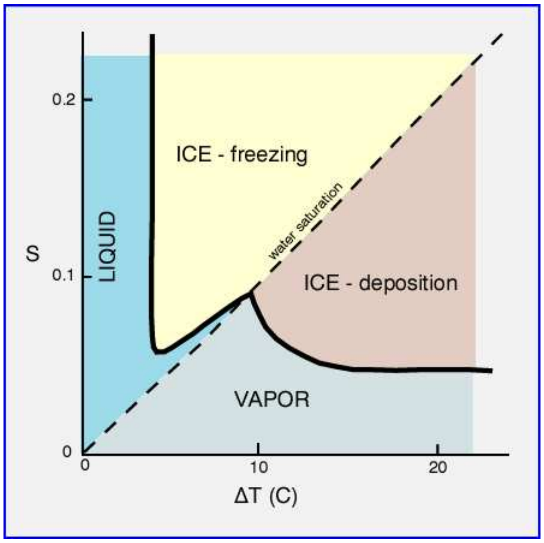


Fig. 7. Thresholds for deposition and for freezing. *S* denotes supersaturation with respect to ice; ΔT is supercooling. (after Manton, 1983)

5. Nucleation active surfaces.

As would be expected, different substrates have different nucleating abilities, the latter being usually expressed as a supersaturation or temperature required for some nucleation rate per unit surface area. Much of ice nucleation research has been dedicated to experiments with varieties of materials, and to the search for explanations why each one would be a good or poor nucleator. The range of materials that have been tested cover inorganic and organic solids, microorganisms, monolayers and more.

One of the basic considerations governing the ice nucleating activities of substances was introduced in 1947 when Vonnegut showed that silver iodide (AgI) was a very effective nucleant in cloud chamber and drop freezing experiments, and ascribed that fact to the similarity between the crystal structure of AgI and hexagonal ice I_h. This extended to ice nucleation research a fact well known for other materials. Another requirement was established at the same time: silver iodide has an extremely small solubility in water. Later work by Vonnegut and colleagues, and by others, confirmed the importance of crystallographic match for effective nucleation with solid solutions whose lattice constants could be varied by changing the proportions of the components. A set of such results in shown in Fig. 8. A totally different set of recent experiments with monolayers of aliphatic long-chain alcohols, to be discussed later, led to the same conclusion.

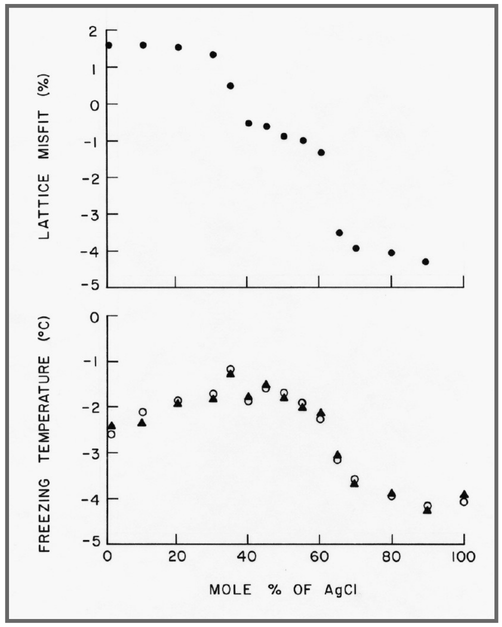


Fig. 8. Freezing is observed to occur at the smallest supercooling for those solid mixtures of AgI and AgCl for which the lattice misfit is the smallest. (From Palanasamy et al, 1986).

The aforesaid should not be interpreted as an overriding or unique factor determining ice nucleating ability. Lattice match may be important but it is neither a necessary nor a sufficient condition. Other factors, by themselves, or in combination with lattice fit, can also lead to good nucleating ability. Interpretations of lattice fit in terms of interfacial energy have been developed but due to difficulties in estimating bonding energies few general and quantitative results emerged.

6. Intractable complications.

As already alluded to as a major difficulty, the most formidable challenge to any theoretical description of heterogeneous ice nucleation is the evidence that specific surface features provide the most likely locations for ice nucleation. The evidence for this fact is most direct for deposition nucleation where the location of ice formation can be directly observed, as illustrated in Fig. 9. While the example shown is for a large surface, not for a submicron aerosol as is likely to be the case for the atmosphere, there is no reason to think that the same phenomenon wouldn't apply. Specific conditions at the locations where ice is seen to form are not known. Steps of the substrate crystal are a definite possibility, but even along the steps there are nonuniformities of unknown character. Calculations have been made of the energetics of germs on steps, etc., in the sense already discussed for various germ configurations, but there has been little success in showing quantitative agreement. It may be also observed from Fig. 9 that the orientations of the growing crystals follow, to a large extent, some specific direction with respect to the substrate structure.

The photographs in Fig. 9 reveal that the nucleation sites follow patterns set by the substrate, but it still could be argued that chance dictates where along a step, for example, nucleation is to take place. Competition among growing crystals also influences where they can develop to observable sizes. The specificity of nucleation sites is shown perhaps even more convincingly by the observations of Anderson and Hallett (1976): on repeated exposures of a surface to supersaturations many ice crystals were seen to form in the same locations. One set of these results are shown in Fig. 10. It may also be noted that nucleation is not repeated on all sites in all tests.

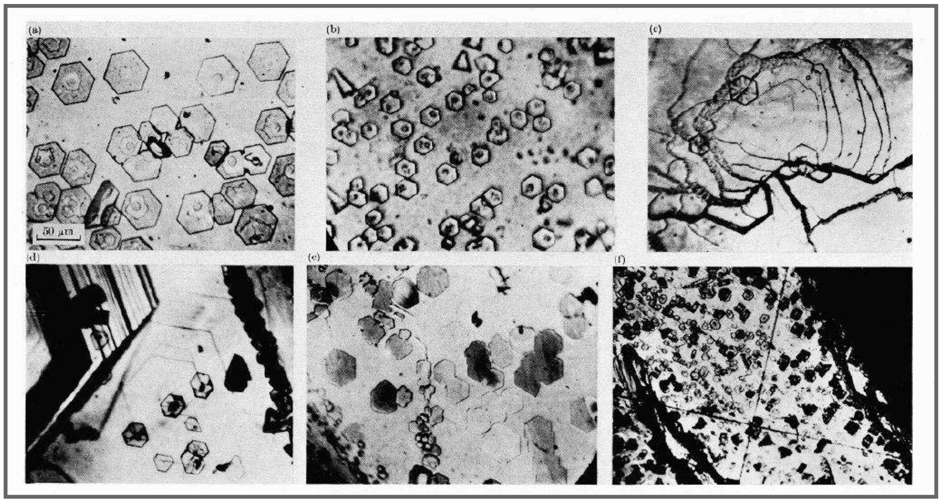


Fig. 9a. Microphotographs of ice crystals nucleated from the vapor on various inorganic substrates. (From Mason, 1957)

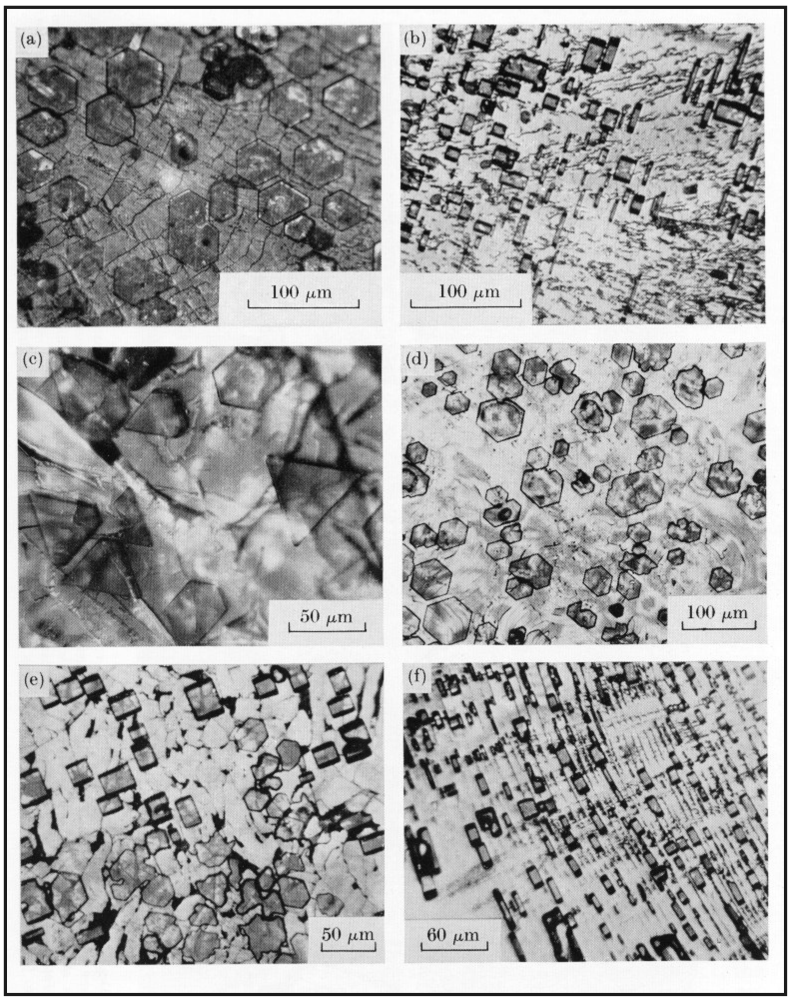


Fig. 9b. Same as Fig. 9a but for organic substrates.

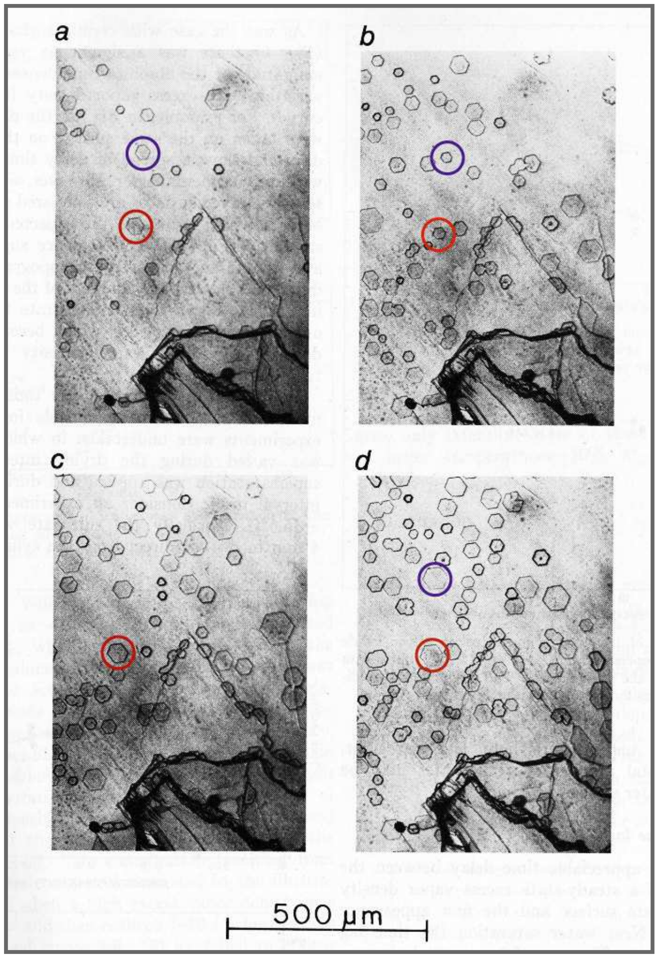


Fig. 10. Repeated exposure of a silver iodide surface at -14C to supersaturations of 5.7, 10, 13 and 17% with respect to ice results in the nucleation of crystals in increasing numbers but with several sites repeatedly becoming activated. Ice was completely evaporated between each observation. The circles identify some of the locations where reactivation is readily observed. (From Anderson and Hallett, 1976)

Evidence for specificity in freezing nucleation is from laboratory experiments in which populations of drops containing heteronuclei are subjected to many cycles of cooling and melting. It is found, that some of the drops repeatedly freeze at or very near the same temperature, consistent with nucleating sites having characteristic temperature of activity, and with a low probability of having more than one site or particle of similar characteristics present in a given drop. The latter part of the foregoing statement holds true for those drops that freeze while the majority of the other drops drawn from the same sample are still unfrozen. Examples of sequences with small variations in freezing temperatures are shown in Fig 11a. However, other drops of the same population may show significant changes in freezing temperatures, as shown in Fig. 11b.

Several conclusions may be drawn at this point. First, that the idea of homogeneous surfaces with a certain probability of nucleation per unit area is, in general, untenable. Surface irregularities, or sites, are the preferred locations of germ development and nucleation, at least in the regions of small supercoolings and low supersaturations that are of major interest. Second, within limitations, the sites can be assigned '*characteristic supersaturations,* S_k' or '*characteristic temperatures*, T_k' , so that the frequency distributions $N(S_k)$ and $N(T_k)$ (per unit area or per particle) are the appropriate descriptors of nucleating activity. These functions are intimately related to the properties of the nucleating surfaces in terms of structure, singularities, etc. Third, fluctuations due to the kinetics of germ growth and decay lead to variations in the activation points of a site in any given test in a

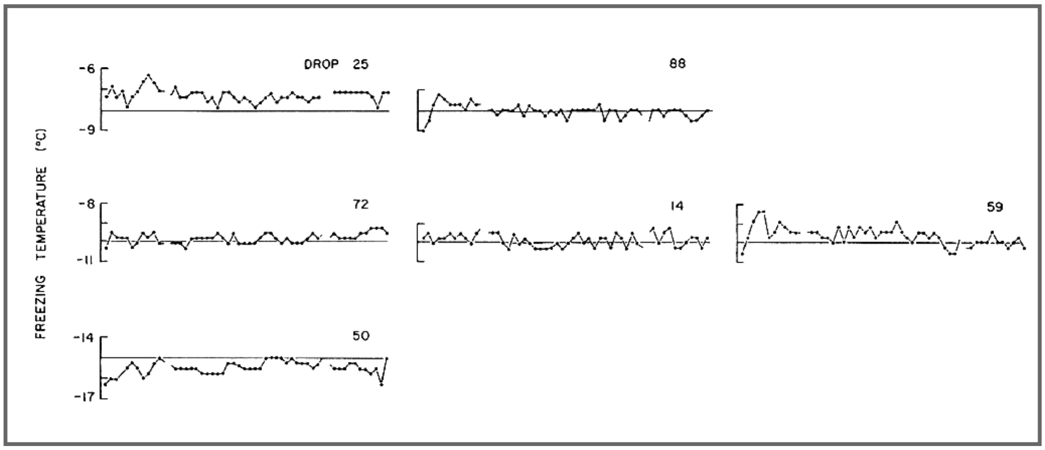


Fig. 11a. Freezing temperatures of selected drops in 114 repeated cycles of cooling and melting. Nucleation temperatures for these drops vary within bands of about 1°C.

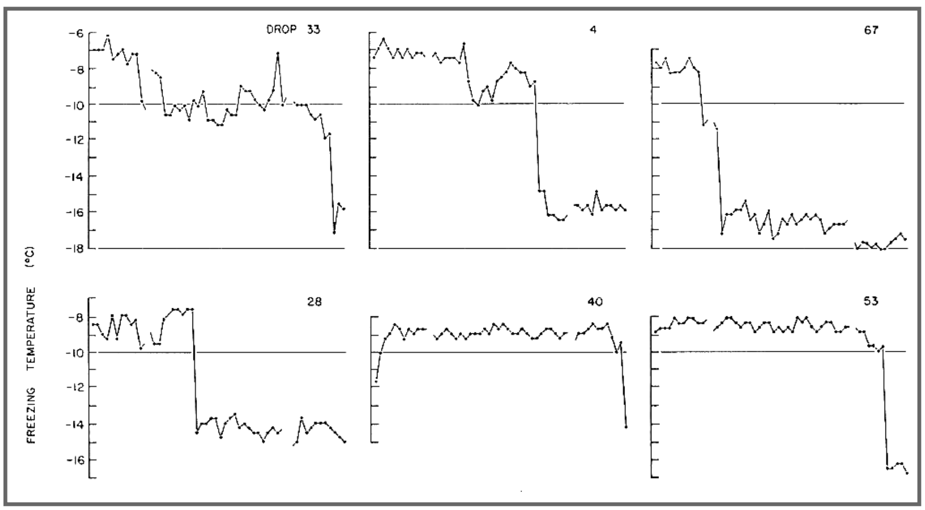


Fig. 11b. In the same sequence of tests as in Fig. 11a, the freezing temperatures of drops here shown exhibited abrupt changes.

probabilistic manner. The magnitudes of these fluctuations are not well known in general, but seem to be small in comparison with the range of values of S_k or T_k that are likely to be found in a population of macroscopically identical samples. The meaning of the qualification just given is not straightforward, so care should be exercised in applying the statement. Fourth, limitations of the use of characteristic values arise from the fact that the sites are not perfectly stable entities but can undergo significant changes when exposed to repeated cycles of nucleation and removal of the ice. The nature of these changes is not well known but can have a number of relatively ready explanations such as deformations caused by the ice formation, contamination from the vapor or liquid parent phase, partial dissolution, etc.

As is evident from the preceding paragraphs, here we are discussing notions rather than quantitative theory. It seems unlikely that a general theory could be formulated to cover the large number of factors involved in heterogeneous ice nucleation. An avenue of progress may lie in the possibility of finding some specific, highly reproducible system, and that sufficient empirical data can be developed to provide descriptive and predictive theories for that system. [This was the hope for many years with AgI, but reality showed it to be a highly variable substance to work with.]

The material in the remainder of this paper is an elaboration of ideas about nucleation sites. The importance of site dimensions in organic materials and the role of crevices in surfaces will be examined.

7. Site dimensions for organic nucleants.

It is evident from the principles discussed in Sections 1 to 3 that the point of nucleation is determined by the chance of formation of a critical size germ. While this idea is difficult to apply in a rigorous way to complex situations presented by the diversity of configurations of nucleation sites on substrates, the general notion is a valid one that the size of the ice germ, and whatever determines that size on the substrate are critical factors. At least three different lines of evidence support this idea specifically. Looking at these findings also serves to demonstrate a number of interesting systems in which ice nucleation has been studied.

7.1 HIGH PRESSURE FORMATION OF ICE ISLANDS IN THE LIQUID

Rather unusual experiments were performed by Evans (1967) with a chamber in which water could be cooled and also exposed to pressures of up to $3{\cdot}10^8$ Pa. The melting point of ice drops to about -35°C at that pressure; thus it was possible to expose thermodynamically stable liquid water to temperatures well below zero 0°C at high

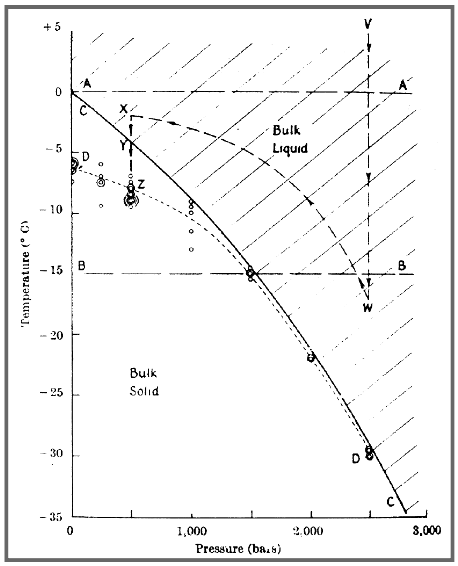


Fig. 12. The phase diagram of ice and the results of nucleation tests with phloroglucinol dihydrate. (From Evans, 1967.)

pressures. With phloroglucinol dihydrate as the nucleating material dispersed in the water, initial tests in which the sample was cooled at various pressures led to the nucleating temperatures along line DZD in Fig. 12. If the sample was cooled to below -15°C along line VW, then warmed to X, subsequent cooling at any pressure produced freezing at essentially zero supercooling, i.e. right along the melting curve CC. This was interpreted by Evans as indicating that a monolayer of ice formed in the liquid below -15°C, and that macroscopic ice could form on that monolayer without a further energy barrier. By varying the lowest temperature in the liquid (point W) in the range 0 to -15°C, it was found that the nucleation temperatures varied between CC and DD. This finding was interpreted as indicating the formation of partial monolayers in patches whose sizes changed in parallel with the depth of cooling at W. In all sequences, if the warmest temperature reached (point X) was above +1°C nucleation temperatures dropped to DD. This is consistent with the melting of the ice patches. In total, while, admittedly, the evidence for the interpretation in terms of ice patches of varying sizes is not very strong, the idea is appealing and suggestive, specially if it is extended or generalized somewhat from ice monolayer patches to regions of ice bonding by a substrate.

7.2 ALCOHOL MONOLAYERS.

Quite startling results were obtained by Gavish et al. (1990), Popovitz-Biro et al. (1994) and Majewski et al. (1994) with monolayers of aliphatic long-chain alcohols ($C_nH_{2n+1}OH$) on water. Drops covered by these monolayers were observed to freeze at small supercoolings, in such a way that the longer the chain length was (larger n) the less the supercooling became. For n=31 freezing was observed with less than 1°C supercooling. Furthermore, temperatures were higher for odd values of n than for even values of n. These results are shown by the zigzag line in Fig. 13. That these results are specific to the aliphatic alcohol monolayers is demonstrated

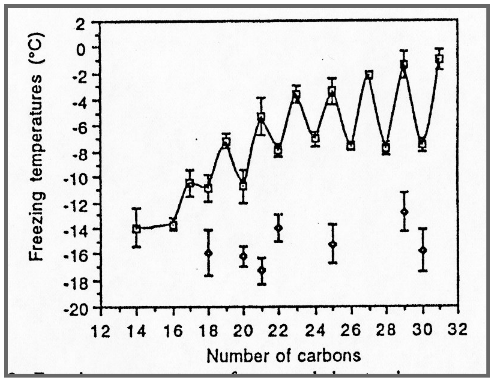


Fig. 13. Freezing temperatures for drops covered by monolayers of aliphatic alcohols ( ) and carboxylic acids (◆) of different chain lengths. (From Popovitz-Biro et al., 1994)

by the comparison with the carboxylic acid series which gave nucleation temperatures of around -16°C regardless of chain length or carbon parity.

Much associated work with these alcohols, including grazing incidence x-ray diffraction studies near 0°C, led to the conclusions that nucleation activity with the monolayers is related to good lattice match, and that with increasing chain length there is an increase in the coherence length of crystal domains. For the most active monolayer the coherence length was determined to be about 25Å, giving a measure of the critical size of the ice germ for near -2°C.

7.3 BACTERIAL NUCLEANTS

The ability of certain bacteria to serve as freezing nuclei at small supercoolings was discovered in the mid-70's. There are about a dozen species of bacteria with this property, all of them epiphytic species (living on the surfaces of plant leafs). They have a role in causing frost damage to crops and in limiting the winter survival of insects; they are used in artificial snow making; and their study led to some important basic results. It was established that ice nucleation is caused by protein molecules in the outer membrane of the bacteria; the ability to produce these proteins can be genetically transferred from active species to non-active ones, or can be eliminated by removal of the appropriate genes. A good summary of these topics can be found in Lee, Warren and Gusta (1995).

Experimenting with four different species of ice nucleating bacteria, Govindarajan and Lindow (1988) exposed the bacteria to different doses of γ-radiation prior to determining their freezing nucleus spectra. Using conventional target theory, which relates radiation dosage to the molecular weight that remains undamaged, they found that the relationship between nucleation temperature and molecular weight was nearly identical for four bacterial species tested. These results are shown in Fig. 14. The first panel shows how increasing radiation dosage changes the shape of the cumulative nucleus spectra. Molecular weight for activity in different 1°C intervals was deduced from the dosage required to reduce nucleus concentrations at those temperatures to 37% of the original value. These molecular weights are shown as a function of nucleation temperature in the second panel of Fig. 14.

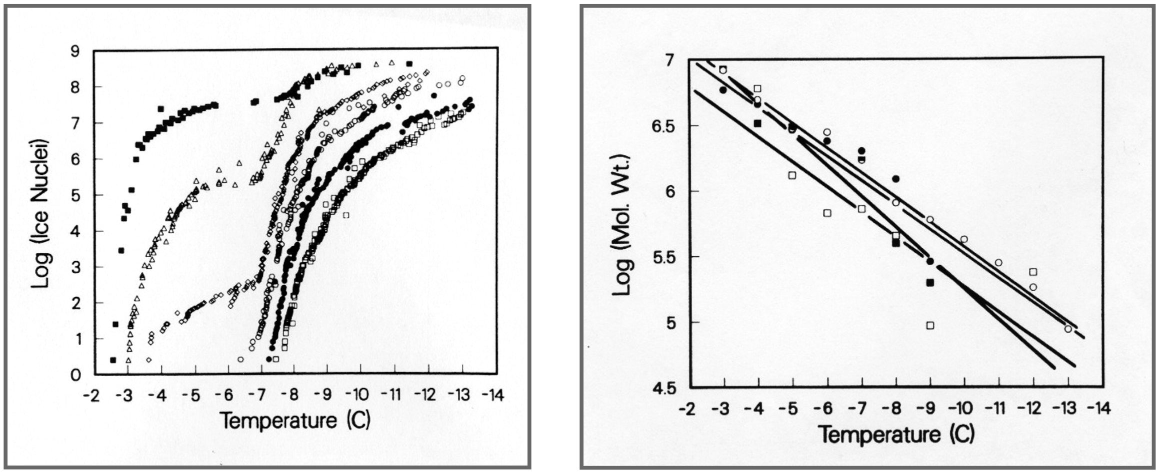


Fig. 14. The left-hand diagram shows how in one of the bacterial samples the concentration of freezing nuclei is gradually reduced (from ■ to □) when radiation dosage is increased from 0.85 to 10.5 Mrad. The right-hand diagram shows the relationship between the estimated undamaged molecular weights and the corresponding freezing temperatures for four different species of bacteria. (From Govindarajan and Lindow, 1988)

The results are shown here in terms of molecular weight, but when thinking of structures embedded in the outer membrane of the bacterial cells it is also consistent with the data to view the sizes in terms of oligomers of smaller macromolecular constituents or in terms of coherence length for undisrupted structural regions. It is not clear at this point which view better represent the nucleation sites. However, it is clear that there is a fairly robust relationship between the sizes of the sites and their nucleation temperatures, with the expected rapid increase in size as 0°C is approached.

Evidence from all three of the systems discussed in Sections 7.1, 7.2 and 7.3 points to the importance of the sizes of the nucleating sites in determining their activity. While there is no reason to expect a universal quantitative relationship to hold for all three of these and yet other materials, it may be concluded that the sizes of the sites are directly related to the sizes of the ice germs forming on them and hence to the temperatures at which the nucleation probability reaches some appropriate level in each set of observations.

8. Confined ice germs

A large variety of experiments with heterogeneous ice nucleation led to findings of hysteresis effects, i.e. increases in nucleating ability resulting from previous ice formation on the samples. These phenomena have been variously called pre-activation or conditioning or memory effects. Here we'll present two such results and suggest that the most likely explanation connecting them is the retention of ice germs in cavities or cracks in the substrate surface. Further evidence for the role of cracks is then presented from a third set of experiments.

8.1 Mineral particles

Particles of several minerals were subjected to controlled temperature and humidity conditions under a microscope by Roberts and Hallett (1968). In the initial tests threshold values were determined as the points at which a small fraction of the particles initiated ice formation. Then, the temperature was lowered sufficiently to cause ice to form on all particles. Threshold determinations were then repeated after the ice was evaporated by exposure to dry air. A systematic difference was found between the initial and subsequent tests, as shown in Fig. 15 for kaolinite. Similarly to the zones depicted in Fig. 7 water saturation was required for ice nucleation at higher temperatures, while a minimum supersaturation was required at lower temperatures. After the first ice formation, both the temperature limit for freezing and the saturation value needed for deposition decreased. The results were quite similar for all five minerals tested.

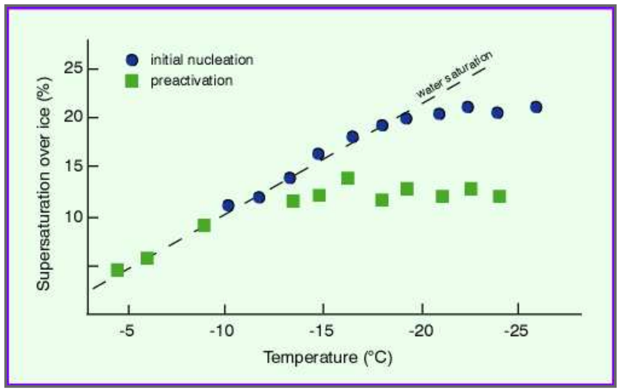


Fig. 15. Changes in temperatures and supersaturations needed for ice nucleation as a result of previous ice formation on kaolinite particles. (From Roberts and Hallett, 1968)

8.2 MERCURIC IODIDE

Memory effects can survive even after warming the sample to above the melting point of ice. This was shown by Edwards, Evans and Zipper (1970) with mercuric iodide, HgI_2, and interpreted in terms of monolayers of ice, similarly to what was discussed in Section 7.1. Further tests with HgI_2 (Vali, 1992) led to the results shown in Fig. 16. In agreement with Edwards, Evans and Zipper, the memory effect was found to survive to +4°C and resulted

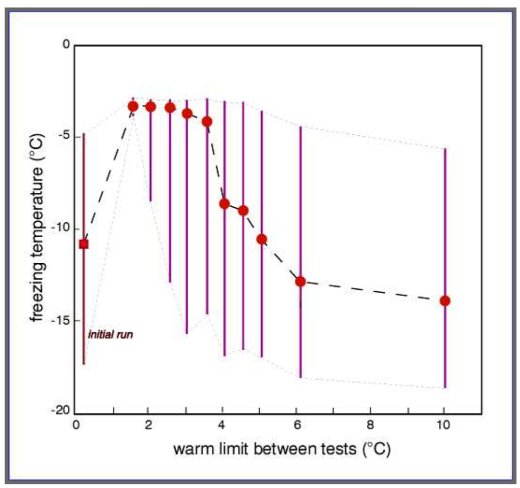


Fig. 16. Mean freezing temperatures (●) and ranges are shown for 99 drops containing HgI_2 particles. The drops were subjected to repeated cycles of cooling until all drops froze and then warmed to the positive temperature limits indicated on the abscissa. (From Vali, 1992)

in raising freezing temperatures from -12°C to -3°C. However, because there was no sharp cold limit to which the sample had to be cooled in order to have a memory effect, and based on the magnitude of the supercooling needed for nucleation after the initial tests, the most likely explanation for the results is not the formation of monolayers but the retention of ice in cracks and cavities on the HgI_2 surface.

Retention of ice in cavities to positive temperatures, and to below ice saturation, may be viewed in general terms as arising from the large contact area and potential for bonding with the substrate relative to the volume of the captive ice, and relative to the small surface are of contact between the ice and the liquid or vapor. Negative (concave) curvature of the interface between the captive ice and the vapor provides a thermodynamic model for the situation with an equilibrium vapor pressure lower than that with respect to a plain ice surface.

8.3 CRYSTAL POLARITY

While it is unquestionable that crystal structure is an important determinant of ice nucleating ability, one of the most striking counter-examples to that role is presented by comparisons of the activities of amino acid isomers. It has been known since the 1960's that the racemic (D,L) and the chiral-resolved (L) pairs of α-amino acids have freezing temperatures that differ by 3° to 5°C even though they have nearly identical crystal structures. Re-examination of the phenomenon by Gavish et al. (1992) led to the recognition of the role that crystal polarity plays. The racemic isomers have layers of alternate orientation parallel to the plate face of the crystal in seven amino acids and for these the chiral-resolved pairs have layers of uniform orientation with respect to the plate face. The former are non-polar and the latter are polar. The combination reverses in two other amino acids. The nucleation tests revealed that in all cases, the polar isomers were more active. This finding led to the interpretation that electric fields in surface cracks of the polar crystals facilitate ice nucleation. The idea is illustrated in Fig. 17. It was also suggested by Gavish et al. that the mechanism of electric fields in cracks can have more general importance for ice nucleation.

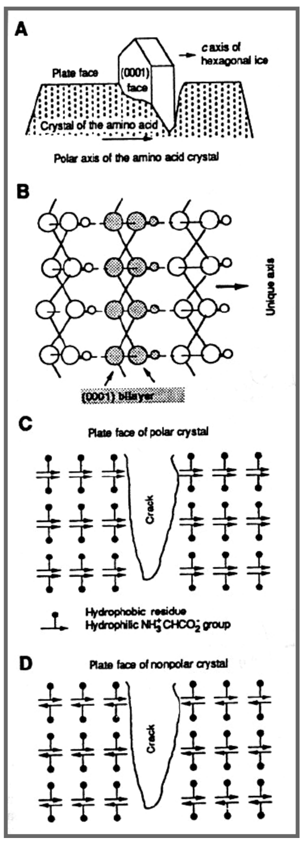


Fig. 17. A - hexagonal ice crystal emerging from the plate face of an amino acid crystal; B - proton ordering assumed along the c-axis of ice can lead to a polar axis; C - for a polar crystal opposing faces of a crack expose different groups; D - for the non-polar crystal the opposing faces are equivalent. (From Gavish et al. 1992)

9. Solute effects in heterogeneous nucleation

The effects of dissolved substances on homogeneous nucleation were discussed in Section 3.2. Not to leave that topic without mention for heterogeneous nucleation, at least a brief comment is in order.

It was seen in the homogeneous case that the effects of solutes go beyond the change of the equilibrium melting point and also influence the probability of germ formation. The result is a further depression of the nucleation rate or of the threshold temperature for homogeneous freezing.

Experiments with diverse substrates and solutions showed that the situation for heterogeneous nucleation differs from the homogeneous case in that the solute may either decrease or increase the supercooling required for nucleation (beyond the melting point depression). Decreases are far more frequent than increases and their magnitudes change monotonically with solute concentration for some nucleants. The effect is less ordered for other nucleants, AgI being one example of highly variable responses.

Interpretation of the observations is clearly not straightforward, as there are now three different factors to consider. The melting point depression is the most basic and for the low concentrations of the nucleant normally dealt with there is no difference expected due to some combined effect of solute and nucleant. Second, the effect on water structure is likely to be fundamentally the same as for homogeneous nucleation except for some secondary differences due to the different temperatures of interest. Third, it appears that the solute might change the properties of the substrate. Possibilities are adsorption onto the surface, partial dissolution of the surface, and others.

10. More possibilities.

There are several other aspects of ice nucleation that would deserve discussion, but they would lead into details beyond the aim of this paper. Just to list a few of the topics regarding heterogeneous nucleating activity: time lags; electric field and charges; surface changes induced by radiation; adsorbed molecules; mixed particle composition.

Regarding ice nucleation in the atmosphere, there are indications that more 'modes' need to be considered than were included in Fig. 6. Some of these possibilities are shown in Fig. 18, and are relatively self-explanatory. Not much is known yet about their importance.

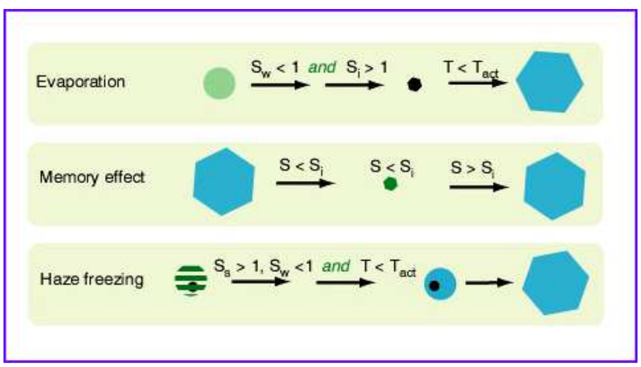


Fig. 18. Further possible modes of atmospheric ice nucleation.

Of course, one should not lose sight of the fact that there are only two basic processes of ice formation: deposition and freezing. The other modes, those in Figs. 6 and 18, are sequences that either change the condition of the nucleating particle, or alter the way the particle and the supercooled cloud droplet interact. Moving from these concepts to established atmospheric relevance will only be possible via observation and experimentation. As already discussed, there is an obvious and tight link between understanding atmospheric ice nucleation processes and the approaches taken in measuring ice nucleus concentrations.

Acknowledgements: Charles Knight and William Cooper are thanked for organizing the 1999 Summer Colloquium and for inviting me to talk about ice nucleation theory. I am grateful to Marcia Baker and Neil Bacon for pointing out a number of places where the text needed clarification.

References

Anderson, B. J. and J. Hallett, 1976: Supersaturation and time dependence of ice nucleation from the vapor on single crystal substrates. *J. Atmos. Sci.,* **33,** 822-832.

Butorin, G. T. and V. P. Skripov, 1972: Crystallization of supercooled water. *Soviet Phys. - Cryst.,* **17,** 322-326.

Cooper, W. A., 1974: A possible mechanism for contact nucleation. *J. Atmos. Sci.,* **31,** 1832-1837.

DeMott, P. J. and D. C. Rogers, 1990: Freezing nucleation rates of dilute solution droplets measured between -30º and -40ºC in laboratory simulations of natural clouds. *J. Atmos. Sci.,* **47,** 1056-1064.

Edwards, G. R., L. F. Evans and A. F. Zipper, 1970: Two-dimensional phase changes in water adsorbed on ice-nucleating substrates. *Trans. Faraday Soc.,* **66,** 220-234.

Evans, L. F., 1967: Two-dimensional nucleation of ice. *Nature,* **213,** 384-385.

Gavish, M., R. Popovitzbiro, M. Lahav and L. Leiserowitz, 1990: Ice nucleation by alcohols arranged in monolayers at the surface of water drops. *Science,* **250,** 973-975.

Gavish, M., J. L. Wang, M. Eisenstein, M. Lahav and L. Leiserowitz, 1992: The role of crystal polarity in alpha-amino acid crystals for induced nucleation of ice. *Science,* **256,** 815-818.

Götz, G., Mészáros, E., and Vali, G., 1991: *Atmospheric Particles and Nuclei.* Akadémiai Kiadó, Budapest. (ISBN 963-05-5682-0)

Govindarajan, A. G. and S. E. Lindow, 1988: Size of bacterial ice-nucleation sites measured in situ by radiation inactivation analysis. *Proc. Natl. Acad. Sci. USA,* **85,** 1334-1338.

Hagen, D. E., R. J. Anderson and J. L. Kassner Jr., 1981: Homogeneous condensation - freezing nucleation rate measurements for small water droplets in an expansion cloud chamber. *J. Atmos. Sci.,* **38,** 1236-1243.

Huang, J. and L. S. Bartell, 1995: Kinetics of homogeneous nucleation in the freezing of large water clusters. *J. Phys. Chem.,* **99,** 3924-3931.

Jeffery, C. A. and P. H. Austin, 1997: Homogeneous nucleation of supercooled water: Results from a new equation of state. *J. Geophys. Res. - Atmosph.,* **102,** 25269-25279.

Knight, C. A., 1979: Ice nucleation in the atmosphere. *Adv. Coll. Int. Sci.,* **10,** 369-395.

Lee, R. E. Jr., Warren, G. J., and Gusta, L. V., 1995: *Biological Ice Nucleation and Its Applications.* APS Press, The American Phytopathological Society, St. Paul, Minnesota.

Majewski, J., R. Popovitzbiro, K. Kjaer, J. Alsnielsen, M. Lahav and L. Leiserowitz, 1994: Toward a determination of the critical size of ice nuclei - a demonstration by grazing incidence X-ray diffraction of epitaxial growth of ice under the $C_{31}H_{63}OH$ alcohol monolayer. *J. Phys. Chem.,* **98,** 4087-4093.

Manton, M. J., 1983: Parameterization of ice nucletion on insoluble particles. *Tellus,* **35B,** 275-283.

Mason, B. J., 1971 : *The Physics of Clouds .* Clarendon Press, Oxford.

Palanisamy M., K. Thangaraj, R. Gobinathan and P. Ramasamy, 1986: X-ray diffraction and ice nucleation studies of AgI-AgCl solid solutions. *J. Cryst. Growth,* **79,** 1005-1009.

Popovitzbiro, R., J. L. Wang, J. Majewski, E. Shavit, L. Leiserowitz and M. Lahav, 1994: Induced freezing of supercooled water into ice by self-assembled crystalline monolayers of amphiphilic alcohols at the air-water interface. *J. Amer. Chem. Soc.,* **116,** 1179-1191.

Pruppacher, H. R., 1995: A new look at homogeneous ice nucleation in supercooled water drops. *J. Atmos. Sci.,* **52,** 1924-1933.

Pruppacher, H. R. and Klett, J. D., 1997: *Microphysics of Clouds and Precipitation - Second Edition.* Kluwer Academic Publ., Dordrecht. (ISBN 0-7923-4211-9)

Roberts, P. and J. Hallett, 1968: A laboratory study of the ice nucleating properties of some mineral particulates. *Quart. J. Roy. Meteorol. Soc.,* **94,** 25-34.

Schaller, R. C. and N. Fukuta, 1979: Ice nucleation by aerosol particles: experimental studies using a wedge-shaped ice thermal diffusion chamber. *J. Atmos. Sci.,* **36,** 1788-1802.

Tabazadeh, A., E. J. Jensen and O. B. Toon, 1997: A model description for cirrus cloud nucleation from homogeneous freezing of sulfate aerosol. *J. Geophys. Res. - Atmosph.,* **102,** 23,845-23,850.

Vali, G., 1992.: *Memory effect in ice nucleation on mercuric iodide*, in "Nucleation and Atmospheric Aerosols", Fukuta, N. and P. E. Wagner (Ed.), A. Deepak Publ. pp. 259-262.

Wood G. R. and A. G. Walton, 1970: Homogeneous nucleation kinetics of ice from water. *J. Appl. Phys.,* **41,** 3027-3026.

Young, K. C., 1993: *Microphysical Processes in Clouds.* Oxford Univ. Press, New York. (ISBN 0-19-507563-3).