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Parameterization of ice nucleation on insoluble particles

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ABSTRACT

Ice nucleation on an insoluble particle is controlled by one of three limiting processes: sublimation, condensation and freezing (contact and immersion). The limiting process is determined by the supersaturation S and supercooling ΔT of the environment, and so nucleation occurs in three distinct regions of $(\Delta T, S)$ space. Within each region, the nucleation of large particles takes place at specified threshold values of ΔT and S. The threshold conditions depend upon three surface parameters, which are related to the contact angle between the nucleus substrate and the phases of water. As ΔT and S are raised above the threshold conditions, small particles are gradually nucleated. Thus the heterogeneous nucleation of ice can be specified in terms of the environmental conditions, ΔT and S, and the surface properties of the nuclei.

1. Introduction

Homogeneous nucleation of ice is unlikely to occur below the upper troposphere and so the initial formation of ice is generally associated with the properties of aerosols on which heterogeneous nucleation can occur. Although soluble components can affect nucleation (Reischel and Vali, 1975) the basic element of ice nucleation is an insoluble particle with a molecular structure comparable to that of ice. In order to predict the initial distribution of ice in a cloud it is therefore necessary to know at least the concentration of such particles in the air and the conditions under which they are activated as ice nuclei (IN).

Measurements from cloud chambers and drop-freezing experiments imply that the concentration of IN increases exponentially with the degree of supercooling. These observations are often used to provide a simple parameterization of ice nucleation in numerical cloud models (e.g. Plooster and Fukuta, 1975). On the other hand, laboratory measurements of nucleation near or below water saturation show that the concentration of IN varies with the kth power of the supersaturation with respect to ice, where the value of k is of order 3. Because the presence of cloud condensation nuclei in clouds ensures that the supersaturation with respect to water barely exceeds zero, these observations of the supersaturation dependence of IN may sometimes be more applicable to the atmosphere than the temperature dependence results. Thus Scott and Hobbs (1977) specify the natural IN concentration in terms of the ice supersaturation for their numerical model of convective cloud.

It would seem that the parameterization of ice nucleation can be chosen somewhat arbitrarily. The ambiguity arises because nucleation can occur through different physical processes. For a given situation, the appropriate nucleation process is determined by the given temperature and supersaturation. The purpose of the present work is to provide a basis for the development of a simple parameterization of ice nucleation in terms of the temperature and supersaturation.

Heterogeneous ice nucleation occurs by sublimation or by condensation-freezing above water saturation. The freezing of supercooled water drops is included in the latter case. (The mechanism for contact nucleation is not well understood (Pruppacher and Klett, 1978) and it is not considered explicitly in the present work.) Isono and Ishizaka (1972) point out that for a given material there is a threshold supersaturation with respect to ice that must be exceeded for sublimation nucleation to occur, and a threshold temperature below which

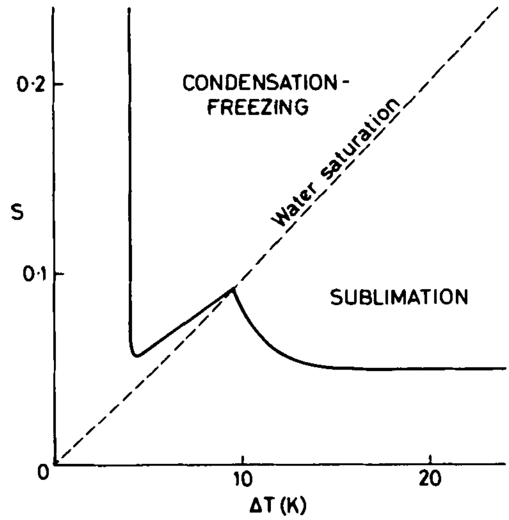

Fig. 1. Typical threshold curve for ice nucleation observed by Schaller and Fukuta (1979), where S is the supersaturation with respect to ice and ΔT is the degree of supercooling.

freezing takes place. These observations are put into a theoretical context by Fukuta and Schaller (1982), who show that condensation-freezing requires the joint probability of a condensation event followed by freezing. Thus they explain the nucleation curves (Fig. 1) observed by Schaller and Fukuta (1979).

2. Limiting processes

When the environment is subsaturated with respect to water, ice nucleation on insoluble particles can occur only by sublimation or condensation-freezing. If J_s is the rate at which nucleation occurs on a particle by sublimation and J_c is the nucleation rate for condensation then the condition for sublimation to be the dominant process is simply that J_s is greater than J_c. The boundary $J_s = J_c$ must lie above the saturation curve for water, as shown in Fig. 2. When the supersaturation with respect to ice S is above this boundary, nucleation happens by condensation-freezing. The overall rate for this two-stage process is determined by the slower process (Fukuta and Schaller, 1982). Thus, if J_f is the nucleation rate for the freezing of a water droplet then the curve $J_c = J_f$ marks the boundary above which nucleation is limited by the rate of formation of ice embryos in water droplets. Below this curve, J_c is less than J_f and the overall nucleation rate is limited by the rate of condensation on the aerosols.

In order to describe the full process of nucleation it is necessary to derive analytical expressions for these boundary curves in terms of the surface properties of the IN. The nucleation rates J_s, J_c and J_f can be derived from the classical statistical theory, discussed by Fletcher (1962). While following the classical theory we reduce the complexity of the algebra by making some further assumptions. In particular we assume that the supersaturation with respect to ice and water, S and S_w, are invariably small compared with unity. Because the threshold of nucleation corresponds to the activation of large particles we also take the radius of an IN to be large compared with the critical radius for an ice embryo.

The sublimation nucleation rate J_s for a large insoluble IN of radius r is given by

$$J_s = \pi r_{*s}^2\, p(2\pi M_0 kT)^{-1/2}\, n_s \exp(-\Delta G_s/kT), \quad (2.1)$$

where

$$\Delta G_s = (\pi/3)\, r_{*s}^2\, \sigma_{iv}(2 + m_s)(1 - m_s)^2,$$

$$r_{*s} = 2\sigma_{iv}/\rho_i RT \ln(1 + S),$$

$$m_s = (\sigma_{sv} - \sigma_{is})/\sigma_{iv}.$$

r_{*s} is the critical radius for an ice embryo in water vapour, p is the vapour pressure, M_0 is the mass of a water molecule, k is the Boltzmann's constant, T is the temperature, n_s is the number of vapour molecules on the entire surface of the IN, ΔG_s is the critical free energy of the embryo, σ_{iv} is the surface free energy between ice and water vapour (105 erg cm^{-2}), ρ_i is the density of ice, R is the specific gas constant for water vapour, m_s is the cosine of the angle of contact of ice on the nucleus surface, σ_{sv} is the surface free energy between the IN substrate and water vapour and σ_{is} is the surface free energy between the substrate and ice. The first terms on the right-hand side of (2.1) represent the rate at which vapour molecules strike an embryo forming on the IN. The vapour pressure is related to the supersaturation by the equation

$$p = (1 + S)\, p_0 \exp\{-L_s/RT_0)(\Delta T/T)\}, \quad (2.2)$$

where

$$\Delta T = T_0 - T.$$

L_s is the latent heat of sublimation and p_0 is the saturation vapour pressure over ice (6.11 mb) at temperature T_0 (273.2 K). The Clausius–Clapeyron equation is used in (2.2) by neglecting the temperature dependence of L_s.

An estimate of n_s is found by equating the rate of arrival of molecules from the vapour to the rate of evaporation of adsorbed molecules from the surface (Pruppacher and Klett, 1978) and so we take

$$n_s = 4\pi r^2 p(2\pi M_0 kT)^{-1/2} v^{-1} \exp(\Delta F_s/kT), \quad (2.3)$$

where v is the vibration frequency of the surface molecules (9×10^{13} s^{-1}) and ΔF_s is the free energy of adsorption per molecule (4.6×10^{-13} erg). Thus the nucleation rate J_s is given by (2.1)–(2.3) in terms of the environmental conditions, S and ΔT, and the IN properties, r and m_s.

Nucleation in the atmosphere can occur only on IN that have a value of m_s near unity. We therefore approximate the critical free energy by

$$\Delta G_s = \pi r_{*s}^2 \sigma_{iv} \varepsilon_s^2. \quad (2.4)$$

where

$$\varepsilon_s = m_s - 1.$$

Ice nucleation generally occurs in the atmosphere over a limited temperature range below the freezing point and for small values of S. We therefore set T equal to T_0 in (2.1)–(2.4) and retain only the leading terms in S and $\Delta T/T$. Thus the nucleation rate for sublimation may be approximated by the equation

$$J_s = a_s(r^2/S^2) \exp(-286.64\varepsilon_s^2/S^2), \quad (2.5)$$

where

$$a_s = 1.60 \times 10^{14}\ \mathrm{s^{-1}}\ \mu\mathrm{m^{-2}}.$$

For given values of J_s, r and ε_s, equation (2.5) is generally satisfied by two values of S. This anomaly is caused by the neglect of S from (2.2) and hence by the omission of a factor $(1 + S)^2$ on the right-hand side of (2.5). The valid solution of (2.5) corresponds to small S. For example, we see that nucleation ($J_s = 1$ s^{-1}) of large particles ($r \gtrsim 0.1$ μm) happens over the supersaturation range of about 4% to 5% when ε_s is 0.015, which is consistent with the more detailed calculation of Fukuta and Schaller (1982).

The statistical theory for condensation on an insoluble particle is identical to the analysis of sublimation, except that parameters relating to ice are replaced by those for liquid water (Fletcher, 1962). Hence the conditions for condensation are approximated by an equation similar to (2.5); in particular, we find that the nucleation rate J_c on a large particle of radius r is given by

$$J_c = a_c(r^2/S_w^2) \exp(-91.19\varepsilon_c^2/S_w^2), \quad (2.6)$$

where

$$a_c = 7.10 \times 10^{13}\ \mathrm{s^{-1}}\ \mu\mathrm{m^{-2}}.$$

The surface parameter ε_c is represented by

$$\varepsilon_c = 1 - m_c, \quad (2.7)$$

where

$$m_c = (\sigma_{sv} - \sigma_{sw})/\sigma_{wv},$$

σ_{sw} is the surface free energy between the substrate of the IN and water, and σ_{wv} is the surface free energy between water and water vapour (76 erg cm^{-2}). Using the Clausius–Clapeyron equation we find that S and the supersaturation S_w with respect to water are related by the equation

$$S = S_w + (\Delta L/RT_0)(\Delta T/T), \quad (2.8)$$

where ΔL is the difference between the latent heat of sublimation and vaporization. Eq. (2.8) is derived by neglecting the temperature dependence of the latent heats and by assuming that both S and S_w are small.

The nucleation rate J_f for freezing on a large IN of radius r is estimated by

$$J_f = (kT/h) \exp(-\Delta F/kT)\, n_f \times \exp(-\Delta G_f/kT), \quad (2.9)$$

where h is Planck's constant, n_f is the number of water molecules on the surface of the IN, ΔF is the activation energy for the diffusion of molecules in the water (4×10^{-13} erg) and ΔG_f is the critical free energy for an embryo. An estimate of n_f is given by the number of molecules in a monolayer adjacent to the surface of the nucleus and so we take

$$n_f = 4\pi r^2(\rho_w/M_0)^{2/3},$$

where ρ_w is the density of water. Thus the nucleation rate is found to be

$$J_f = a_f r^2 \exp\{-0.938\varepsilon_f^2(\Delta T/T_0)^{-2}\}, \quad (2.10)$$

where

$a_f = 1.83 \times 10^{16}\ \mathrm{s^{-1}}\ \mu\mathrm{m^{-2}}$.

The surface parameter ε_f is defined by

$$\varepsilon_f = 1 - m_f, \tag{2.11}$$

where

$m_f = (\sigma_{sw} - \sigma_{is})/\sigma_{iw}$,

and σ_{iw} is the surface energy between water and ice (29 erg cm^{-2}).

Using eqs. (2.5), (2.6) and (2.10) we can now determine the boundary curves in Fig. 2 in terms of the surface parameters ε_s, ε_c and ε_f of the IN. The r dependence of J_f is different from that of J_c and J_s, and so we arbitrarily consider the nucleation of a particle with radius 1 μm. It is readily shown that the exponentials dominate the nucleation rates. Thus the boundary curve $J_s = J_c$ is well approximated from (2.6), (2.8) and (2.9) by the equation

$$S = 2.54(\Delta T/T)/\{1 - 0.564(\varepsilon_c/\varepsilon_s)\}. \tag{2.12}$$

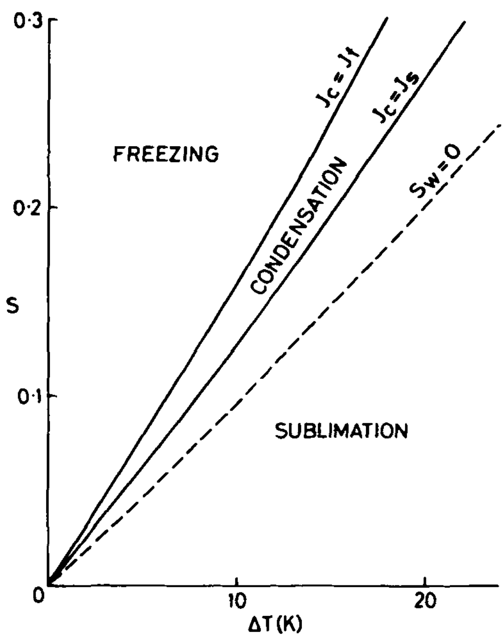

Fig. 2. Regions of (ΔT, S) space for the limiting processes for ice nucleation; S and S_w are the supersaturations with respect to ice and water, ΔT is the degree of supercooling, and J_s, J_c and J_f are the nucleation rates for sublimation, condensation and freezing.

Similarly the boundary curve $J_c = J_f$ is found from (2.6) and (2.10) to be

$$S = \{9.86(\varepsilon_c/\varepsilon_f) + 2.54\}\ (\Delta T/T). \tag{2.13}$$

The curve (2.12) defines the boundary between nucleation by sublimation and that by condensation freezing. In the region above (2.12), but below (2.13), the rate of condensation of water on the particles limits the overall nucleation rate. However, if

$$2.54/\{1 - 0.564(\varepsilon_c/\varepsilon_s)\} > 2.54 + 9.86(\varepsilon_c/\varepsilon_f), \tag{2.14}$$

then the curve $J_c = J_f$ must be omitted from Fig. 2, because the overall rate of nucleation for condensation freezing is everywhere limited by the rate of freezing.

The manner in which nucleation occurs at a given point in (ΔT, S) space is seen to be controlled by the three surface parameters of the IN. Now eqs. (2.1), (2.7) and (2.11) imply that these parameters are not independent; in particular, we find that

$$\sigma_{iv}\,\varepsilon_s = \sigma_{wv}\,\varepsilon_c + \sigma_{iw}\,\varepsilon_f.$$

Applying the observation (Pruppacher and Klett, 1978),

$$\sigma_{iv} = \sigma_{wv} + \sigma_{iw},$$

we see that the surface parameters for a given substrate are related by the equation

$$\varepsilon_s = 0.72\varepsilon_c + 0.28\varepsilon_f. \tag{2.15}$$

Therefore only two of the surface parameters are independent.

3. Threshold conditions

For any point in (ΔT, S) space, the rate of nucleation of ice is limited by sublimation, condensation or freezing, as shown in Fig. 2. Within each limiting region the rate of nucleation of large particles is governed by either eq. (2.5), (2.6) or (2.10), and so nucleation in each region can be considered independently. The exponential term in each nucleation equation ensures that the nucleation rate varies very rapidly with S or ΔT. If nucleation is defined to occur when the nucleation rate equals J then the value of S or ΔT at nucleation is clearly not sensitive to J. It is usual to take $J = 1\ s^{-1}$ (Fletcher, 1962). The dominance of the exponential also implies that the conditions for nucleation are insensitive to the particle radius r. Thus all large IN are nucleated over a narrow range of S or ΔT (Fletcher, 1962). It is therefore appropriate to define a threshold supersaturation S_1 or supercooling ΔT_1 for nucleation, and we arbitrarily take the threshold to correspond to $r = 1$ μm.

In the region below $J_c = J_s$ in Fig. 2, ice nucleation on insoluble particles takes place by sublimation, and the rate of nucleation J_s for a particle of radius r is specified by (2.5). Fig. 3 shows the relationship between the supersaturation S at nucleation and the surface parameter ε_s, calculated from (2.5) with $J_s = 1\ s^{-1}$ and $r = 1\ \mu$m. It is clear that over the range of interest in the atmosphere, the threshold supersaturation S may be approximated by

$$S_1 = 2.82\varepsilon_s. \qquad (3.1)$$

Eq. (3.1) specifies the supersaturation with respect to ice at which nucleation by sublimation occurs on large IN with a surface parameter ε_s. Thus we characterize a distribution of IN by the single parameter ε_s, which is related to the angle of contact of the ice interface on a particle.

Near water saturation, the limiting process for ice nucleation in the condensation-freezing mode is the rate of condensation of water on the insoluble

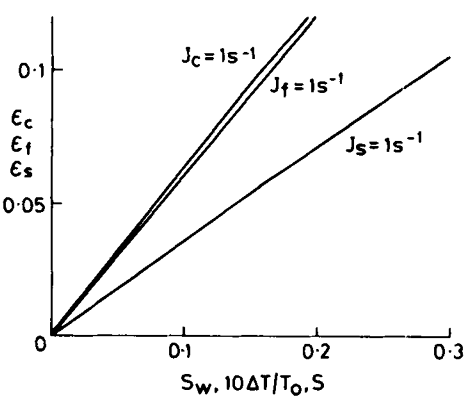

Fig. 3. Nucleation curves for condensation, freezing and sublimation on an insoluble particle of radius 1 μm, from eqs. (2.6), (2.10) and (2.5).

nucleus. In the region between the curves $J_c = J_s$ and $J_c = J_f$ on Fig. 2, the rate of ice nucleation is therefore approximated by (2.6). Fig. 3 shows the nucleation curve, defined by $J_c = 1\ s^{-1}$ and $r = 1$ μm, for condensation near water saturation. It is seen from Fig. 3 and (2.8) that the threshold supersaturation S_1 can be estimated by the equation

$$S_1 = 1.60\varepsilon_c + 2.54(\Delta T/T). \qquad (3.2)$$

Eq. (3.2) relates the threshold for the nucleation of large particles to the characteristic surface parameter ε_c of the IN when the limiting process is condensation.

Under most conditions above water saturation the limiting process for ice nucleation is the rate of freezing of a condensed water droplet. This region lies above the curve $J_c = J_f$ in Fig. 2, where (2.1) yields the ice nucleation rate. The nucleation curve ($J_f = 1\ s^{-1}$ and $r = 1\ \mu$m) is seen from Fig. 3 to be given by

$$\Delta T_1/T_0 = 0.158\varepsilon_f, \qquad (3.3)$$

where ΔT_1 is the threshold supercooling at which large particles are nucleated. Thus the temperature threshold for freezing nucleation is given in terms of the characteristic surface parameter ε_f.

The threshold conditions (3.1)–(3.3) can be combined with the limiting boundaries (2.5), (2.6) and (2.10) to define the regions in (ΔT, S) space where ice nucleation can occur. The nucleation regions are determined by the three surface parameters ε_c, ε_f and ε_s. The values of these parameters are not known for most IN, but they can be inferred from the observed threshold conditions. Fletcher (1962) states that condensation occurs on silver iodide particles at a supersaturation with respect to water of 2.5%. It follows from (2.8) and (3.2) that ε_c for AgI is equal to 0.016. This value of ε_c corresponds to a contact angle of 10°, in agreement with direct observations (Fletcher, 1962). The freezing threshold for AgI is at the supercooling ΔT_1 of 4 K (Hobbs, 1974). Eq. (3.3) shows that ε_f for AgI is therefore 0.093 and the corresponding contact angle is 25°. Using the compatibility condition (2.15) we now find that the parameter ε_s for AgI must equal 0.038. This value of ε_s implies from (2.8) and (3.1) that sublimation at water saturation occurs at a supercooling of 11 K, which is consistent with the observed supercooling of 12 K (Hobbs, 1974).

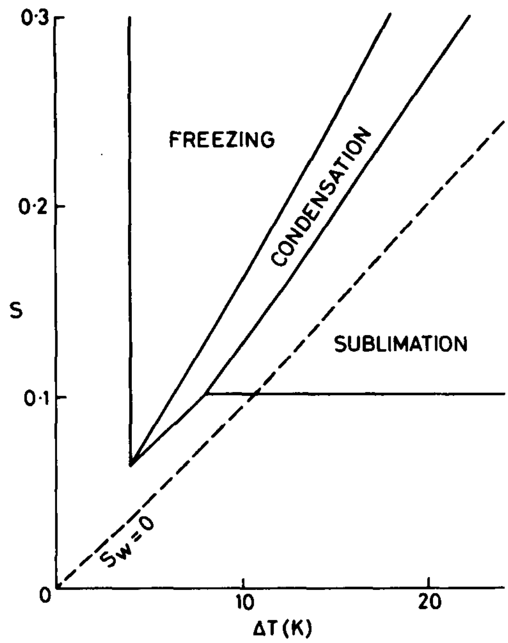

Fig. 4. Regions in $(\Delta T, S)$ space where ice nucleation can occur on insoluble particles with $\varepsilon_c = 0.016$, $\varepsilon_f = 0.093$ and $\varepsilon_s = 0.038$; S is the supersaturation with respect to ice, ΔT is the degree of supercooling and S_w is the supersaturation with respect to water.

The surface parameters for silver iodide can therefore be represented by $\varepsilon_s = 0.038$, $\varepsilon_c = 0.016$ and $\varepsilon_f = 0.093$. Since condition (2.14) is not satisfied, there is a distinct region in $(\Delta T, S)$ space where condensation is the limiting nucleation process for AgI. Fig. 4 shows the regions in which ice nucleation on AgI can take place.

4. Nucleation of small particles

The nucleation equations (2.5), (2.6) and (2.10) are derived under the assumption that the radius of the IN is much larger than the critical radius of an ice embryo. Fletcher (1962) discusses a correction to these equations that takes into account the radius of the IN. The analysis considers the geometry of an embryo forming a spherical cap in contact with the particle, so that an embryo of critical radius r_* requires a relatively small volume. However, the volume of an embryo of radius r_* on a particle of radius less than r_* is minimized if the embryo completely encloses the particle rather than

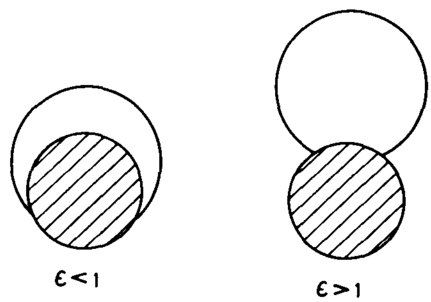

Fig. 5. Spherical cap of radius r_* on a particle (hatched) of radius less than r_*. Angle of contact is determined by surface parameter ε.

forming a cap when the surface parameters ε_s, ε_c and ε_f are small, as shown in Fig. 5. If an embryo encloses a particle then a critically sized embryo of negligible volume can be formed when the particle radius is equal to r_*.

The preceding discussion suggests that all IN of radius larger than the critical radius r_* should be nucleated when the threshold conditions are exceeded. Thus small IN should be gradually nucleated after the initial burst of large IN at the threshold. In order to model the manner in which small particles are nucleated, we assume that nucleation takes place precisely when the particle radius r equals the critical radius of an ice embryo r_*.

Using (2.1) we now find that nucleation of a small IN of radius r occurs at the supersaturation S given by

$$S = \left(\frac{T_0}{T}\right)\left(\frac{r_{0s}}{r}\right), \tag{4.1}$$

where $r_{0s} = 2\sigma_{iv}/\rho_i R T_0$, which is about 1.8×10^{-3} μm. Eq. (4.1) shows a weak dependence upon temperature, but the essential feature is that the radius of a particle varies inversely with the supersaturation at which it is nucleated by sublimation.

It is seen from Fig. 6 that (3.1) and (4.1) can be combined to predict the supersaturation S required to nucleate an IN of radius r. The surface properties of the distribution of IN are characterized by the single parameter ε_s. When S is less than S_1, given by (3.1), there is no nucleation. When S increases above S_1, the number of activated IN increases as smaller particles are nucleated. Although this model is a crude ap-

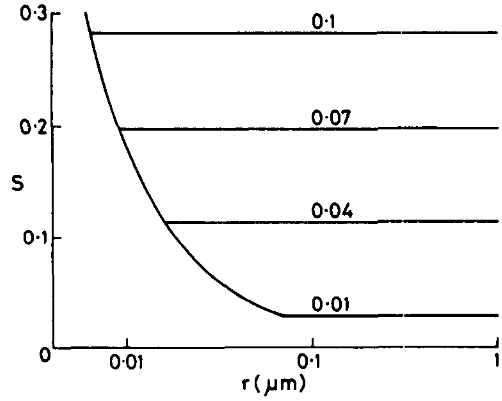

Fig. 6. Supersaturation S required to nucleate a particle of radius r by sublimation. Numbers refer to the surface parameter ε_s.

proximation to the full classical theory discussed by Fletcher (1962), it includes the essence of the physics and allows the process to be readily parameterized.

Measurements of the concentration of sublimation IN in the atmosphere show a power-law relationship between the concentration N and the supersaturation (Huffman, 1973); in particular,

$$N = cS^k, \tag{4.2}$$

where c and k are constants. Such measurements are generally taken near water saturation so that the ice supersaturation S is expected to be above the threshold value S_1. Then increasing the supersaturation causes particles of radius r, given by (4.1), to be nucleated. Putting (4.1) into (4.2) we see that the concentration of IN with radius greater than r is given by

$$N = c\left(\frac{T_o}{T}\right)^k \left(\frac{r_{0s}}{r}\right)^k. \tag{4.3}$$

Eq. (4.3) shows a weak dependence of N upon temperature.

The main prediction of (4.3) is that the concentration of IN follows a power law. Observations in rural and urban conditions by Zamurs and Jiusto (1982) indicate that the constant k in (4.2) has a value of about 3. This result applied to (4.3) implies that the concentration of IN has the same functional behaviour as the Junge distribution (e.g. Twomey, 1978), which represents the total aerosol concentration in the atmosphere. On the other hand, the constant c in (4.3) is typically 0.1 cm^{-3} while the total aerosol concentration for particles greater than 0.1 μm is of order 10^3 cm^{-3}. Thus the size distribution of IN is expected to represent a uniform fraction of about 10^{-9} of the distribution of the total aerosol in the atmosphere.

The value of the exponent k in (4.2) is found to be considerably larger than 3 for artificially generated aerosols and for polluted air masses (Huffman, 1973). A large value of k corresponds to a sharp cut-off in the size distribution in (4.3) and so is consistent with the presence of a particular source of small particles.

An estimate of the conditions under which small particles are nucleated by condensation is found by assuming that they are nucleated when the IN radius equals the critical radius r_{*c} for a water embryo. The radius r_{*c} is related to the water supersaturation S_w by (Fletcher, 1962)

$$r_{*c} = 2\sigma_{wv}/\rho_w RT \ln(1 + S_w), \tag{4.4}$$

where ρ_w is the density of water. Using (2.8) we see that above the threshold S_1 a small particle of radius r is nucleated at the ice supersaturation S given by

$$S = (T_0/T)(r_{0c}/r) + 2.54(\Delta T/T), \tag{4.5}$$

where $r_{0c} = 2\sigma_{wv}/\rho_w RT_0$, which is about 1.2×10^{-3} μm.

Ice nucleation in the condensation-limited region of Fig. 2 is described by eqs. (3.2) and (4.5). Large IN are nucleated when the supersaturation reaches the threshold S_1. Increasing the supersaturation leads to the gradual nucleation of smaller IN, specified by (4.5).

We assume that small particles are nucleated by freezing when their size equals the critical radius r_{*f} for an ice embryo, where (Fletcher, 1962)

$$r_{*f} = 2\sigma_{iw} T_0/\rho_i \Delta L \,\Delta T. \tag{4.6}$$

Hence a small IN of radius r becomes nucleated when the supercooling is given by

$$\Delta T/T_0 = r_{0f}/r, \tag{4.7}$$

where $r_{0f} = 2\sigma_{iw}/\rho_i \Delta L$, which is about 2.0×10^{-4} μm. Eq. (4.7) implies that particles of radius 0.005 μm are nucleated at a temperature of -10 °C. This is consistent with the observation by Vali (1966) that a large fraction of IN with radius less than 0.01 μm are active above -10 °C.

Nucleation in the freezing-limited region of (ΔT, S)-space is seen from (3.3) and (4.7) to be independent of the supersaturation. At the threshold supercooling ΔT_1 the large IN are activated and smaller particles nucleate as the temperature decreases.

Many observations of freezing water drops and of particle nucleation at high supersaturations indicate that the concentration N of freezing nuclei is specified over a limited range of supercooling by the equation (Pruppacher and Klett, 1978)

$$N = N_0 \exp (b \, \Delta T), \tag{4.8}$$

where N_0 is of order 4.5×10^{-8} cm^{-3} and b is about 0.5 K^{-1}. Provided that ΔT is above the threshold ΔT_1, eqs. (4.7) and (4.8) can be combined to predict the size distribution for freezing IN. Then we find that the IN concentration is given by

$$N = N_0 \exp (r_0/r), \tag{4.9}$$

where r_0 is about 2.5×10^{-2} μm.

Comparison of (4.9) to (4.3) with $k = 3$ suggests that the concentrations of sublimation and freezing nuclei in the atmosphere are similar for particles greater than about 0.25 μm. However, the freezing nucleus size distribution (4.9) has a sharp cut-off near $r = r_0$, thus implying that most freezing nuclei are smaller than about 0.01 μm, as suggested by Vali (1966). The distribution of freezing nuclei therefore appears to be more restricted than the distribution of sublimation nuclei, which appears to represent a uniform fraction of the total aerosol.

5. Summary

The preceding analysis allows the nucleation of ice in the atmosphere to be modelled in terms of the surface properties of the ambient insoluble particles. Because the dominant process can be sublimation, condensation or freezing three surface parameters ε_s, ε_c and ε_f must be determined. These parameters are related to the angle of contact between the substrate of the IN and the different phases of water; they are defined in (2.1), (2.4), (2.7) and (2.11). However, eq. (2.15) implies that only two of the surface parameters are independent for a given substrate.

Nucleation limited by sublimation or condensation can take place only above a threshold supersaturation S_1, given by (3.1) and (3.2) in terms of ε_s and ε_c. When freezing is the limiting process, nucleation requires a minimum degree of supercooling ΔT_1, which is specified in (3.8). Fig. 4 shows the region in (ΔT, S) space in which ice nucleation can occur for the case when $\varepsilon_c = 0.016$, $\varepsilon_f = 0.093$ and $\varepsilon_s = 0.038$.

The region in which condensation is the limiting process is bounded by the curves (2.12) and (2.13). It is seen from (2.12), (2.13) and (3.2) that the threshold supersaturation for sublimation is in general larger than the minimum supersaturation at which condensation-freezing can occur, as shown in Fig. 4. Nucleation by sublimation happens just above water saturation while the rate of condensation is limited by the water supersaturation S_w. The extent of the region where sublimation occurs in water supersaturation is limited by the ratio $\varepsilon_c/\varepsilon_s$.

It appears that ice nucleation is generally determined by either the rate of freezing of water ($S_w > 0$) or by the rate of sublimation ($S_w < 0$). All large IN are nucleated at the threshold curves but smaller particles should be activated at higher supersaturations for sublimation or at higher supercoolings for freezing. Thus the observed relations between the concentration of IN and S for sublimation or ΔT for freezing should indicate the size distribution of IN in the atmosphere. By assuming that small particles are nucleated when their size equals the critical radius for an ice embryo, we find that the size distribution of sublimation nuclei (4.3) follows a Junge power-law. This result suggests that sublimation IN are essentially a uniform fraction (of order 10^{-9}) of the total aerosol population in the atmosphere. On the other hand, the size distribution for freezing nuclei (4.9) appears to have a sharp cut-off near 0.01 μm.

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