

A New Look at Homogeneous Ice Nucleation in Supercooled Water Drops

H. R. PRUPPACHER

Institute for Atmospheric Physics, University of Mainz, Mainz, Germany

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ABSTRACT

The classical theory for homogeneous ice nucleation in supercooled water is investigated in the light of recent data published in various physico-chemical journals on the physical properties of supercooled water and in the light of recent evidence that the cooperative nature of the hydrogen bonds between water molecules is responsible for a singularity behavior of pure supercooled water at -45°C .

Recent rates for homogeneous ice nucleation in supercooled water drops derived from field experiments at the cirrus cloud level and from cloud chamber studies were shown to be quantitatively in agreement with the laboratory-derived lowest temperatures to which ultrapure water drops of a given size have been supercooled. Using these verified nucleation rates together with the recent physical property data for supercooled water, the activation energy for the transfer of water molecules across the ice-water interface was computed using the classical nucleation rate equation. The thus computed values are significantly different from earlier values that were based on the activation energy for viscous flow but are consistent with present knowledge of the structure of supercooled water. The present results eliminate the earlier discrepancies that existed between the results of the classical nucleation equation, the field and laboratory data, and the results from the molecular model of Eadie.

1. Introduction

Forty years have now elapsed since McDonald's famous summary article in 1953 on homogeneous ice nucleation in supercooled water drops. In the intervening time new data have become available on the physical behavior of supercooled water. These data allow us to answer the questions still left open at the time of McDonald's article. In his article, McDonald provided a theoretical background to the experimental observation that at temperatures below -30°C the production of ice crystals sharply increases inside supercooled clouds. By applying homogeneous nucleation theory to the nucleation of ice in pure, supercooled water, McDonald was able, at least qualitatively, to explain the sudden increase of the nucleation rate below -30°C . Unfortunately, at the time of McDonald's article [and unfortunately even at the time at which the books of Dufour and Defay (1963) and of Pruppacher and Klett (1978) were published] no firm values were available on the density, viscosity, specific heat, latent heat, and surface tension of supercooled water, nor on the interface energy between water and ice, nor, in particular, on the activation energy for the transfer of water molecules across the ice-water interface—parameters needed to solve the nucleation equation. In particular,

no information was available on how these parameters vary with temperature in the range 0° to below -40°C , although rough extrapolations were available (e.g., *Smithsonian Meteorological Tables*). The currently available data, published in various physico-chemical journals, show that the earlier extrapolations are not sufficiently accurate since at that time it was not known that the parameters that characterize supercooled water would exponentially vary with decreasing temperature below 0°C . Accurate values are, however, importantly needed for a correct description of homogeneous ice nucleation. This mechanism plays a fundamental role in the formation of cirrus clouds and therefore, in turn, in climate modeling. In the present paper we are taking a second look at homogeneous ice nucleation in view of the new data available on the various parameters that characterize supercooled water. In doing so, we further attempt to make the classical model for homogeneous ice nucleation consistent with the molecular model worked out some time ago by Eadie (1971).

2. The classical theory homogeneous ice nucleation in supercooled water

McDonald (1953) made the cloud physics community aware that the so-called well-behaved freezing at 0°C (the temperature of melting ice) is not the rule in the atmosphere. Rather, supercooling of water is a natural phenomena and is thermodynamically as well as kinetically inevitable. This can readily be understood by applying Kelvin's law to the equilibrium of an em-

Corresponding author address: Dr. H. R. Pruppacher, Institut für Physik der Atmosphäre, Fachbereich Physik, Johannes Gutenberg-Universität Mainz, Becherweg 21 Mainz, 55099 Germany.

bryonically small ice particle of radius a_i in an environment of a supercooled aqueous solution drop of radius a_d , which yields (Pruppacher and Klett 1978)

$$-\frac{L_m}{T^2} dT + 2 \left[\frac{M_w}{\rho_w(T)} - \frac{M_w}{\rho_i(T)} \right] d \left[\frac{\sigma_{s/a}(T)}{a_d} \right] - \frac{2M_w}{\rho_i(T)} d \left[\frac{\sigma_{i/s}(T)}{a_i} \right] + RTd \ln a_w = 0, \quad (1)$$

where L_m is the latent heat of melting, T temperature, ρ_w the density of water, ρ_i the density of ice, M_w the molecular weight of water, $\sigma_{s/a}$ the surface tension of a solution drop against air, $\sigma_{i/s}$ the interface energy between ice and aqueous solution, a_d the size of the water drop in which the ice particle is located, a_i the radius of the ice particle, and a_w the activity of water in solution. For the case of pure water and $a_d \gg a_i$, one may integrate this equation by averaging ρ_i as well as L_m over the temperature interval of integration to give

$$\ln \frac{T_0}{T_e} = \frac{2M_w \sigma_{i/lw}}{L_m \rho_i a_i}, \quad (2)$$

where T_e is the temperature at which the ice particle is in equilibrium with the surrounding supercooled water and $\sigma_{i/lw}$ is the interface energy between supercooled water and ice. This equation says that the smaller the embryonic ice particle the larger the supercooling of the water has to be to keep the ice particle in equilibrium. Thus, if nucleation would have to begin on clusters of just a few molecules, the freezing temperature of water would be much lower than that actually observed. Thus, for explaining the phase change from supercooled water to ice, thermodynamic arguments do not suffice. Rather, kinetic effects have to be considered that involve a succession of chance collision of molecules that build up embryonic ice particles large enough to withstand the disruptive action of the thermal motions. Of course, atmospheric aerosol particles present inside water drops may significantly catalyze this kinetic buildup of embryonic ice particles. This is shown in Fig. 1, which demonstrates that most clouds are glaciated once the air temperature has fallen below -20°C . Nevertheless, a small fraction of clouds appears to remain liquid to temperatures as low as -40°C . Thus, supercooled clouds were observed at temperatures as low as -35°C by Weickmann (1949) over Germany and by Borovikov et al. (1963) over Russia, at temperatures as low as -40.7°C , in wave clouds over the Rocky Mountains by Heymsfield and Miloshevich (1993), and at temperatures as low as -38°C at the cirrus cloud level by Heymsfield and Sabin (1989) and Sassen and Dodd (1988).

Of course, such large supercoolings can occur only if the drops are devoid of particles. This is well verified by laboratory studies with single drops and populations of drops of ultrapure water as shown in Fig. 2. For drawing this figure we have reanalyzed a considerable

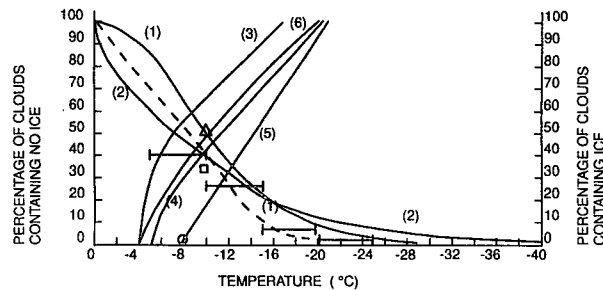


FIG. 1. Percentage of clouds containing no ice (curves 1 and 2 and symbols) and percentage of clouds containing ice (curves 3 to 6). (1) Pepler (1940), (2) Borovikov (1963), (3) Mossop et al. (1970), (4) Morris and Braham (1968), (5) Isaac and Schemenauer (1979), (6) Hobbs (1974), — Sassen (1989), - - - Moss and Johnson (1992), Δ Kosarev et al. (1978), \square Braham (1964), and \circ McPartland et al. (1977).

number of laboratory studies and derived from them the lowest temperature at which drops could be supercooled when exposed to cooling rates typically between 1°C min^{-1} and 1°C s^{-1} . The scatter that one notes is due to the different techniques used to support the drops.

In the absence of aerosol particles, freezing of supercooled water proceeds via homogeneous nucleation at the rate given by Pruppacher and Klett (1978) as

$$J = 2N_c \left(\frac{\rho_w kT}{\rho_i h} \right) \left(\frac{\sigma_{i/lw}}{kT} \right)^{1/2} \times \exp \left(-\frac{\Delta g^\ddagger}{RT} + \frac{\Delta F_g}{kT} \right), \quad (3)$$

where h is Planck's constant, k is Boltzmann's constant, R is the universal gas constant, N_c is the number of water molecules in contact with unit surface area of ice, ΔF_g is the energy per molecule of ice germ formation, and Δg^\ddagger is the activation energy per mole for the transfer of water molecules across the ice-water interface. In all previous publications, values for Δg^\ddagger have been based on values for the activation energy for viscous flow. It will be shown in this paper that such a substitution cannot be reconciled with our present knowledge on the structure of supercooled water and is the main cause for the existing discrepancies between the homogeneous nucleation rates derived from the classical nucleation equation, from field observations at the cirrus cloud level, and from Eades (1971) molecular model. For the case of small supercoolings of only a few degrees ΔF_g can be expressed (Pruppacher and Klett 1978) by

$$\Delta F_g = \frac{16\pi M_w^2 \sigma_{i/lw}^3}{3 [L_m \rho_i \ln(T_0/T)]^2}, \quad (4)$$

in which the densities of ice and the latent heat of melting have been averaged over the temperature interval

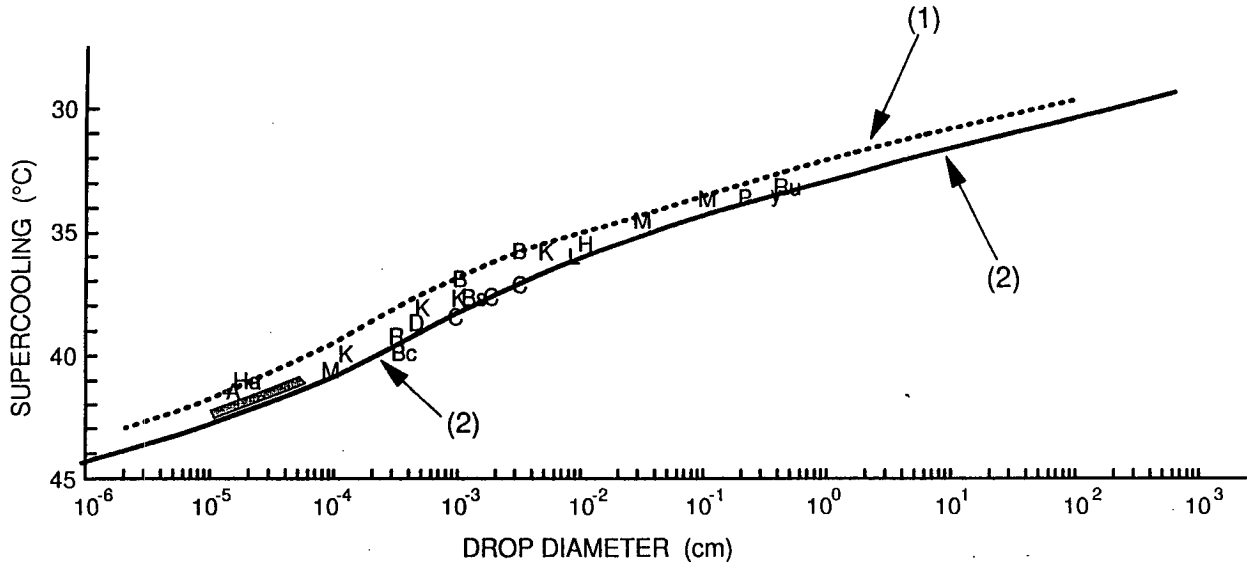


FIG. 2. Lowest temperatures to which extrapure water drops of given size and exposed to cooling rates between $1^{\circ}\text{C min}^{-1}$ and 1°C s^{-1} have been supercooled during laboratory experiments: H (Hoffer 1961), M (Mossop 1955), D (DeMott and Rogers 1990), B (Bigg 1953), P (Pruppacher and Neiburger 1963), L (Langham and Mason 1958), Ha (Hagen et al. 1981), Ru (Rouleau 1958), K (Kuhns and Mason 1968), Y (Bayardelle 1954), R (Rasmussen 1982), A (Anderson et al. 1980), Bs (Butorin and Skripov 1972), and Bc (Broto and Clause 1976). Lines 1 and 2: Temperature at which 99.99% of a population of uniform-sized water drops freezes when exposed to cooling rates of $1^{\circ}\text{C min}^{-1}$ and 1°C s^{-1} , respectively [from Eq. (7) with J values consistent with curve 2 in Fig. 3].

of integration. However, in view of the large supercoolings required for the onset of homogeneous ice nucleation in supercooled water drops of cloud drop size, and in view of the strong variation with temperature of the parameters appearing in Eqs. (3) and (4) (as shall be shown below), an averaging procedure is not justified. Rather the energy of germ formation has to be computed from (see Pruppacher and Klett 1978)

$$\Delta F_g = \frac{\sigma_i / w \Omega_g}{3} \quad (5)$$

with $\Omega_g = 4\pi a_g^2$, wherein the radius a_g of the ice germ consisting of g molecules has to be computed from a numerical integration of Eq. (1).

3. The parameters in the classical nucleation rate equation

At the time of McDonald's article and even up to 1978, values for the parameters that appear in Eqs. (1)–(5) were available only down to 0°C so that values below 0°C had to be obtained by extrapolating the data above 0°C . Using these data, values for the nucleation rate J were computed by Pruppacher and Klett (1978) using the classical theory. These values are plotted as a function of temperature as curve 1 in Fig. 3. Sassen and Dodd (1988) pointed out the discrepancy between the nucleation rates derived by them from aircraft measurements at the cirrus cloud level, the results derived by Pruppacher and Klett (1978) from the classical theory, and the laboratory results of Hagen et al.

(1981). Heymsfield and Sabin (1989), in turn, found consistency between Eadies (1971) molecular statistical model, and the Sassen and Dodd data, however, also pointed to the inconsistency with the classical results.

DeMott and Rogers (1988) pointed out the fair agreement between their cloud chamber results and the observations of Sassen and Dodd and the underpredictions of the classical theory. In their later article, DeMott and Rogers (1990) compared the nucleation rates derived from their cloud chamber studies with those of Butorin and Skripov (1972), derived from the rates of freezing of single drops in oil, and with those of Taborek (1985), derived from emulsified water drops. Although the lowest temperature to which drops could be supercooled by Butorin and Skripov agree well with the other data in Fig. 2, Taborek's nucleation rates derived from freezing times of drops kept at a constant temperature are considerably too low compared to the DeMott and Rogers data. The same applies to the nucleation rates derived by Taborek (1985) from the lifetime of drops at constant temperature of emulsified water in oil-containing surface active chemicals. In addition to various difficulties that arise in conjunction with deriving nucleation rates from drop lifetimes at constant temperature, it is very likely that the surfactants used significantly inhibited the freezing process in the water drops contained in oil. This is evident from Taborek's Fig. 2, in which two different surfactants gave nucleation rates that differed by more than one order of magnitude. Similar conclusions were pointed out by Broto and Clause (1976), who also used surfactants as emulsifiers.

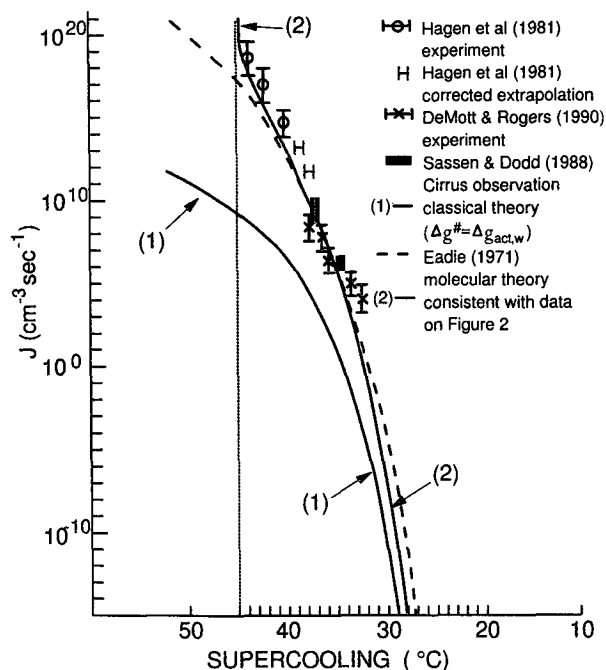


FIG. 3. Variation of the rate of homogeneous ice nucleation in supercooled water. (1) Classical theory based on the values for $\sigma_s, \rho_w, L_m, \rho_w, \rho_i$ prior to 1978 and for $\Delta g^\ddagger = (\Delta g)_{act,w}$. (2) Classical theory based on recent values for $\sigma_s, \rho_w, L_m, \rho_w, \rho_i$, and on Δg^\ddagger given by curve 2 in Fig. 11. Dashed line: molecular model of Eadie (1971). Cloud chamber experiments: \ominus Hagen et al. (1981), \times Hagen et al. (1981) data extrapolated by author to warmer temperatures, \times DeMott and Rogers (1990), and \blacksquare observations at the cirrus cloud level (Sassen and Dodd 1988).

In the 1980s a number of articles appeared in the physico-chemical literature that provide values for the parameters in Eqs. (1)–(4) down to temperatures as low as -35°C . From these data an educated extrapolation to as low as -45°C is possible. The data suggest that supercooled water exhibits an anomalous behavior near -45°C , as exemplified in Figs. 4–10.

The recurring limit at -45°C in the thermodynamic properties of water led Angell (1982) to speculate that this limit represents a singularity reminiscent of the exponential behavior observed for systems approaching phase transitions of higher order. One attempt to explain the fact that supercooled water behaves in many respects as if it were approaching a second-order phase transition has been advanced by Speedy (1982a,b), who proposed that there is a region in the P–V plane bounded by a spinodal curve on which liquid water becomes absolutely unstable. As the spinodal is approached, mean-field theories (Compagner 1972) suggest that the thermodynamic functions diverge. In fact, the mean field analysis of Binder (1984) suggests that the free energy barrier to nucleation behaves similarly to other thermodynamic functions; that is, it should vanish as a power of $T - T_s$, where T_s is the temperature of the spinodal curve. As a reason for the behavior of

supercooled water, Angell suggested that a cooperative process among the water molecules dominates the water structure at low temperature. In analogy to the behavior of other systems he showed that the anomalies of supercooled water can be described by an equation of the form

$$Y = A_y \left(\frac{T}{T_s} - 1 \right)^{-\lambda_y} \quad (6)$$

well known to describe critical phenomena. Equation (6) predicts a rapid increase of the property Y as the temperature T approaches T_s , where A_y and λ_y are parameters chosen to fit the variation of the property Y with temperature, and T_s is the singularity temperature. Angell suggested for water $T_s = 228 \pm 3 \text{ K}$ ($= -45 \pm 3^\circ\text{C}$). We note that T_s is within about 2 K of the lowest temperature to which the smallest observed pure water drops have been found to supercool (see Fig. 2).

Raman spectra of Bansil et al. (1982), Yeh et al. (1982), Hare and Sorensen (1990), d'Arrigo et al. (1981), as well as low-angle X-ray scattering experiments of Bosio et al. (1981), Stanley and Teixeira (1980), and Rice and Sceats (1981) down to temperature as low as -30°C show that the hydrogen bond indeed exhibits a strongly cooperative nature that results in the formation of a network of clusters of molecules with intact hydrogen bonds inside the cluster. Each cluster appears to be bonded to the surrounding clusters by mostly non-hydrogen bond forces. With decreasing temperature the clusters grow increasingly larger. At the same time, the bond links, which are bent at warmer temperatures, become increasingly linear, resulting in an increase of bond energy.

From what has been said above one expects and indeed finds that the fraction p of hydrogen bonds broken with respect to the total number of bonds in supercooled water decreases with decreasing temperature approaching zero near -45°C . This is exemplified in Fig. 4. To be noted is the fact that even at -40°C , where

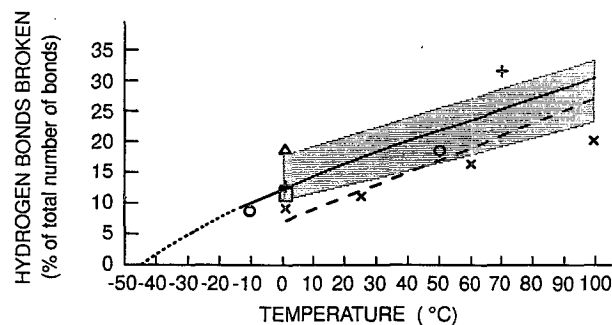


FIG. 4. Variation with temperature of the number of hydrogen bonds broken in water: --- Walrafen (1972), \times Hasted (1972), \circ Luck (1962, 1963, 1965), $+$ from L_m/L_s , Δ Davis and Litovitz (1965), \blacksquare Luck (1967), \square Hindman (1966). Continuous line with dotted extrapolation: currently proposed variation, consistent with the -45°C limit.

only about 1.7% of the total number of bonds are broken, as much as 10^{21} bonds cm^{-3} are broken, considering that at this temperature about 6×10^{22} bonds cm^{-3} are present in supercooled water.

The increased clustering in supercooled water was historically (Angell 1982) first noted in the sharp increase with decreasing temperature of the specific heat (Fig. 5) and the viscosity (Fig. 6) of supercooled water and in the sharp decrease with decreasing temperature of the density (Fig. 7) of supercooled water. Each of these quantities is shown to approach an extreme value as -45°C is approached. It is physically reasonable to assume that, on extrapolation, other properties of supercooled water also will behave similarly. Consistent with the -45°C limit, we have extrapolated the latent heat of melting of ice and the latent heat of evaporation

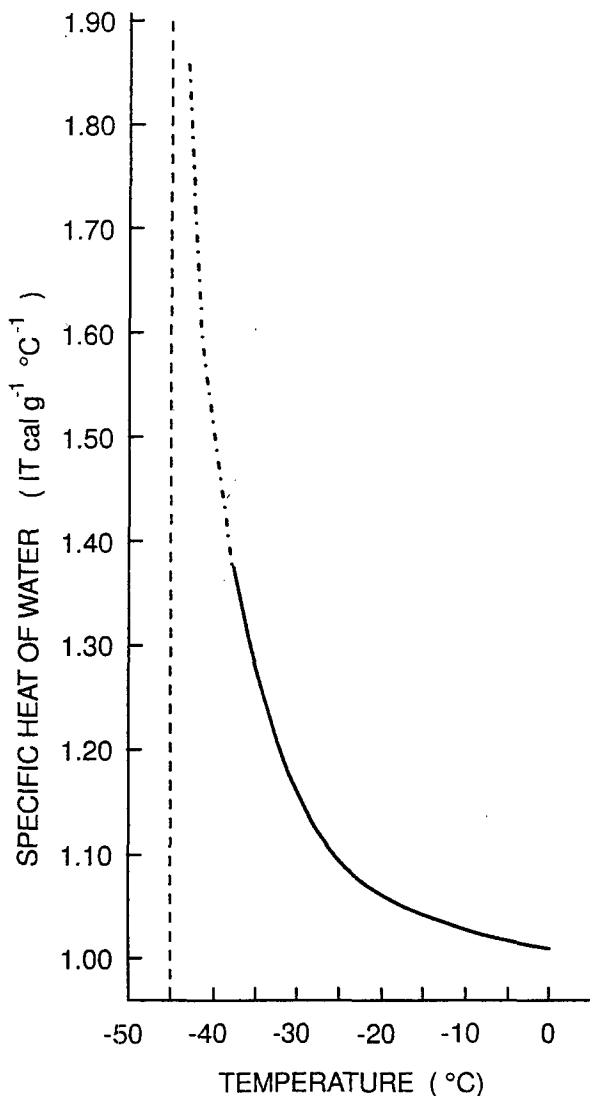


FIG. 5. Variation with temperature of the specific heat c_w of water (Angell et al. 1982), extrapolated to -45°C .

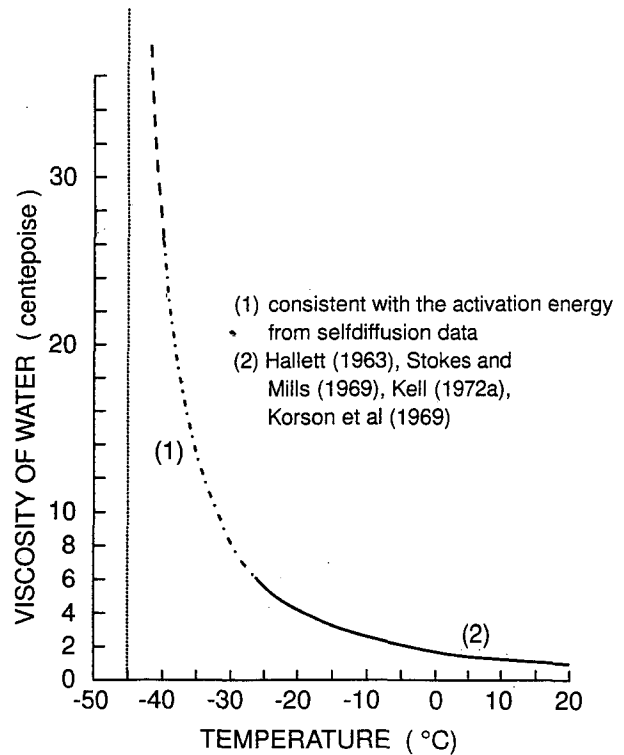


FIG. 6. Variation with temperature of the viscosity of water, extrapolated to -45°C .

of supercooled water (Fig. 8), the surface tension of water (Fig. 9), and the interface energy between water and ice (Fig. 10). Figure 8 is obtained by using the extrapolated values for c_w together with Kirchoff's law $dL_m/dT = c_w(T) - c_i(T)$ and $dL_c/dT = c_{pv} - c_w(T)$.

4. The activation energy for transfer of water molecules across the water-ice interface

Among the parameters that enter the nucleation rate equation [Eqs. (1), (2)] the activation energy Δg^\ddagger for the transfer of water molecules between water and ice has not been discussed yet. Unfortunately, this parameter is not accessible by experiment unless assumptions are made. It therefore has to be obtained indirectly. To do this, the following two steps were followed. In a first step the J values derived from observations at the cirrus cloud level and from expansion cloud chambers were verified against the lowest temperature to which drops of given volume were supercooled under controlled laboratory conditions. In a second step the verified J values were introduced into Eq. (3) together with the values given for ρ_i given by Pruppacher and Klett [1978, Eq. (4-84a)], and for $\rho_w(T)$, $L_m(T)$, and $\sigma_{i/w}(T)$ given by Figs. 7, 8, and 10, respectively, to solve for $\Delta g^\ddagger(T)$.

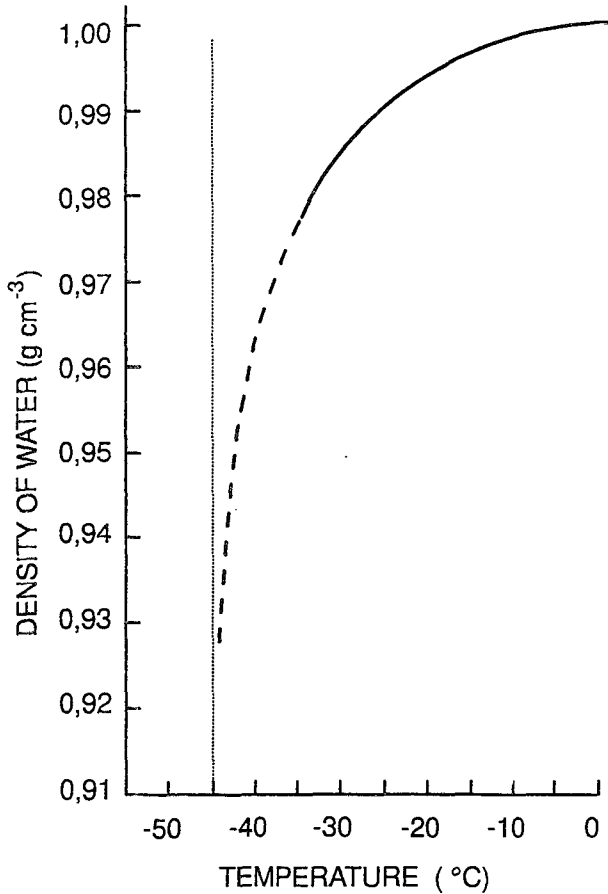


FIG. 7. Variation with temperature of the density of water (Hare and Sorensen 1987), extrapolated to -45°C .

To implement the first step, the J values derived from observation at the cirrus cloud level and from data derived from expansion chambers were fitted to a smooth curve in the range -33° to -44°C , and the obtained J values were introduced into the relation (see Pruppacher and Klett 1978)

$$\int_{T_{99.99}}^{T_0} J(T) dT = 9.21 \frac{\gamma_c}{V_d} \quad (7)$$

From this relation the temperature $T_{99.99}$ at which 99.99% of a population of drops of volume V_d froze when cooled at the rates $1^{\circ}\text{C min}^{-1}$ and 1°C s^{-1} . The contributions to the integral between T_0 and -33°C in Eq. (7) were considered negligible. In this manner curves 1 and 2 in Fig. 2 were obtained. We note that these curves encompass excellently the lowest temperatures to which drops of various sizes were found to be supercooled under laboratory conditions if cooled at rates between $1^{\circ}\text{C min}^{-1}$ and 1°C s^{-1} . The scatter of the experimental data is attributable in part to the different experimental techniques used. This agreement provided a satisfactory verification of the values for the nucleation

rate J introduced into Eq. (7). Curves 1 and 2 in Fig. 2 were then extrapolated to -27°C in order to obtain J values consistent with these data and with the original J values found from Eq. (7). This led to the J values listed in Table 1 and plotted as curve 2 in Fig. 3.

To implement the second step, the obtained J values were now entered into Eq. (3) to solve for the activation energy $\Delta g^{\ddagger}(T)$ for the transfer of water molecules across the ice–water interface, considering Eqs. (1) and (5). By doing so, curve 2 in Fig. 11 and the values listed in Table 2 are obtained. We notice from this curve that below -29°C $\Delta g^{\ddagger}(T)$ decreases with decreasing temperature in agreement with the trend obtained by Hagen et al. (1981) from expansion cloud chamber studies but in contrast to the activation energy $(\Delta g)_{\text{act},w}$ for the diffusion of water molecules through bulk water that exponentially increases with decreasing temperature. It is obvious that by substituting $(\Delta g)_{\text{act},w}$ for $\Delta g^{\ddagger}(T)$ in Eq. (3), as has been done in previous analyses of Eq. (3), values for J will be obtained that are much too low in comparison to the values observed at the cirrus cloud level. On the other hand, a decrease of $\Delta g^{\ddagger}(T)$ with decreasing temperature is not only consistent with field observations at the cirrus cloud level and expansion chamber studies but is, as suggested by Hagen et al. (1981), consistent with what is known about the cluster structure of supercooled water. Thus, with decreasing temperature the freezing process

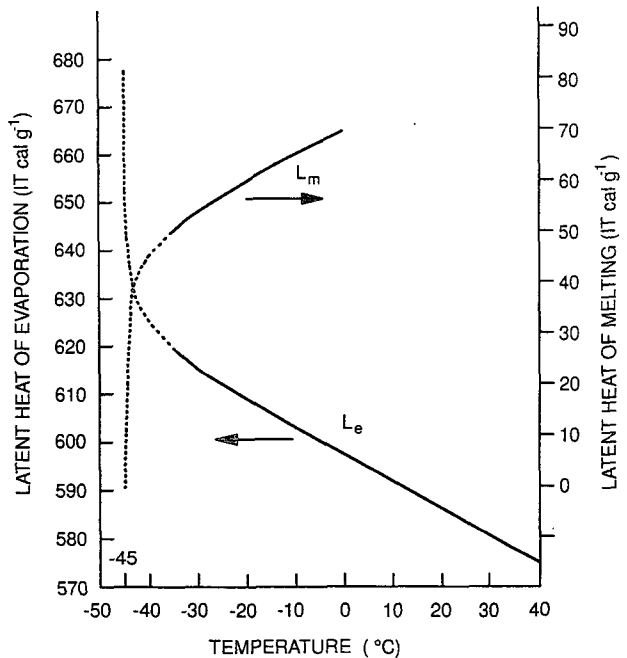


FIG. 8. Variation with temperature of the latent heat of melting and latent heat of evaporation of supercooled water based on values for c_w in Fig. 5, specific heat of ice from Lonsdale (1958) and Ginnings and Corrucini (1947) and Kirchoff's law. Extrapolation is done to be consistent with -45°C limit.

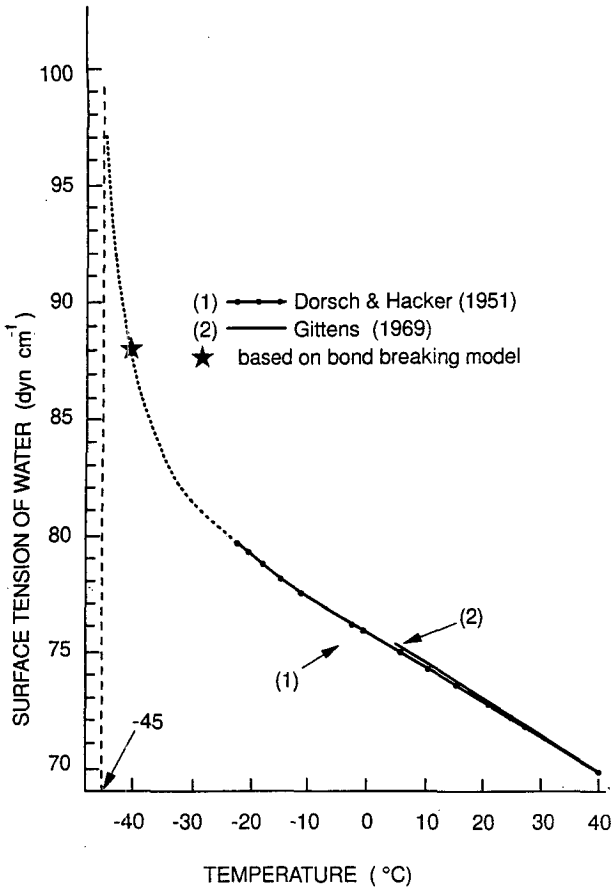


FIG. 9. Variation with temperature of the surface tension of water, extrapolated to be consistent with the -45°C limit.

does *not* involve the transfer of single water molecules across the ice–water interface. Rather, the transfer involves increasingly large clusters of water molecules where hydrogen bonds are broken only at the cluster periphery. This mechanism must result in a decrease of the activation energy for transfer per mole of transferred water, as is verified by curve 2 in Fig. 11.

At temperature warmer than -29°C the transfer of water molecules across the ice–water interface is controlled by the self-diffusion of simple water molecules through bulk water, while at temperatures between -29° and -32°C a transition regime exists in which the mechanism of growth of ice embryos is not well defined.

Since cloud drops are aqueous solution drops, the question may be raised whether at the cirrus cloud level homogeneous ice nucleation in supercooled solution droplets may be computed by simply solving Eq. (3) together with Eq. (5) and the complete form of Eq. (1), using the values for $L_m(T)$, $\rho_i(T)$, $\rho_w(T)$, $\sigma_{i/w}(T)$, and $\Delta g^{\ddagger}(T)$ for pure water. This may indeed be done as long as one can consider that most cloud drops consist of highly dilute solutions. (Usually the concentration of cloud water is less than 10^{-3} mole

liter $^{-1}$.) If computations have to be carried out for drops that consist of more concentrated solutions, the values for $\sigma_{i/w}(T)$ and $\Delta g^{\ddagger}(T)$ given in this paper do *not* apply anymore since the interface energy between water and ice as well as the interface transfer of water molecules, is increasingly affected by salt ions, which become selectively adsorbed at the ice–water interface. The effects of such ion layers on $\sigma_{i/w}$ and Δg^{\ddagger} are not known. It is obvious, however, that the -45°C limit applying to pure water will decrease to a concentration-dependent lower limit.

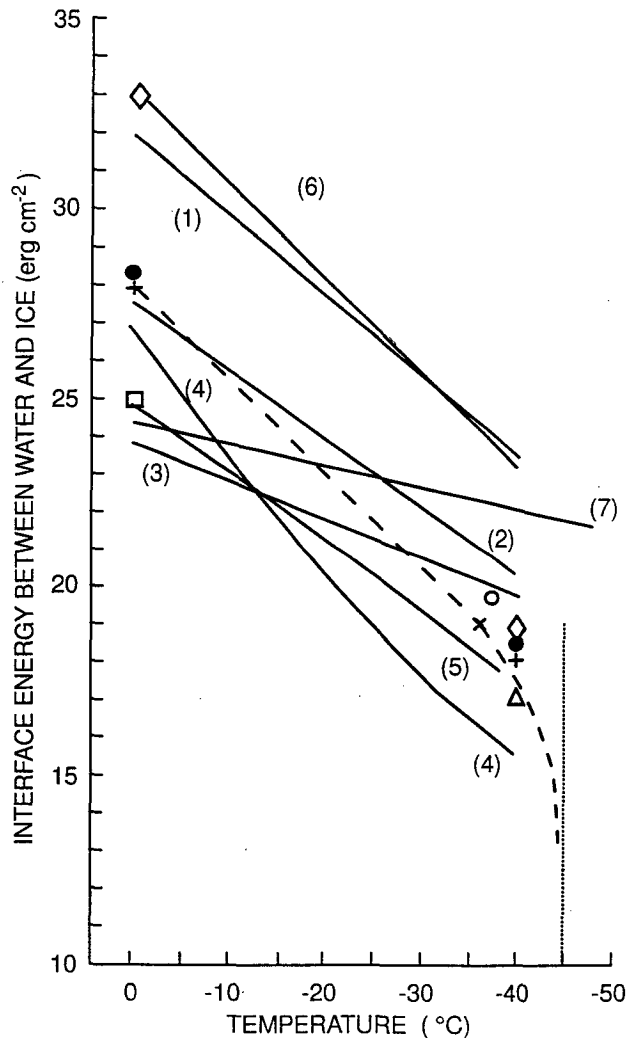


FIG. 10. Variation with temperature of the interface energy between water and ice. (1), (2) Wood and Walton (1970); (3) Dufour and Defay (1963); (4) Rasmussen and MacKenzie (1972); (5) Pruppacher (unpublished manuscript), based on data of Kubelka and Prokscha (1944); (6) Pruppacher (unpublished manuscript), based on data of Turnbull (1950); (7) Eadie (1971); \times Hoffer (1961); \circ Kuhns and Mason (1968); \triangle Mason (1957); \square Coriel et al. (1971); \diamond Ketcham and Hobbs (1969); $+$ Pruppacher (unpublished manuscript), based on Antonovs rule (1977); and \bullet Pruppacher (unpublished manuscript), based on latent heat of melting (1977). The dashed line is the proposed variation, consistent with the -45°C limit.

TABLE 1. Rate of homogeneous ice nucleation in supercooled water.

Supercooling (°C)	J (cm ⁻³ s ⁻¹)
29	46×10^{-11}
30	43×10^{-8}
31	15×10^{-5}
32	65×10^{-3}
33	15×10^0
34	30×10^2
35	20×10^4
36	10×10^6
37	30×10^7
38	50×10^8
39	90×10^9
40	10×10^{11}
41	20×10^{12}
42	10×10^{14}
43	50×10^{15}
44	20×10^{17}

5. The molecular model for homogeneous ice nucleation in supercooled water

In an attempt to avoid solving the classical formulation of the homogeneous nucleation equation that requires a knowledge of the macroscopic parameters down to temperatures of -40°C and below, Eadie (1971) formulated an expression for the energy of ice germ formations in supercooled water by using a statistical approach similar to that used later by Hale and Plummer (1974) for the formation of water and ice germs in supersaturated vapor. Eadie based his approach on the statistical thermodynamic model of water by Nemethy and Sheraga (1962) and Vand and Senior (1965a,b). In a very elaborate piece of work he formulated and evaluated the energy $\Delta\Phi_i$ required for the formation of an ice embryo of i molecules from

$$\frac{\Delta\Phi_i}{kT} = i \ln\left[\left(\sum_{j=0}^4 w_j q_j / N_1\right)\right] - \ln \frac{Z_i}{N_1}, \quad (8)$$

where q_j is the molecular partition function for a j -bonded molecule, the degeneracy factor $w_j = 4!/[(4-j)!j!]$, j is the number of hydrogen bonds emanated by a water molecule, N_1 is the number of single water molecules in the system, and Z_i is the molecular partition function for a cluster of i water molecules. Eadie determined q_j from available data for the hydrogen bond energy in water and for the vibrational, translational, and rotational motion of the water molecule in water. For determining Z_i Eadie assumed an icelike geometry for the embryos of i molecules. Then Z_i was calculated from the number of doubly, triply, and quadruply bonded molecules in an embryo; from the number of broken bonds on the surface of an embryo; from the molecular partition function q_j (with $j = 2, 3, \text{ or } 4$); and from the molecular partition function for ice. A plot of $\Delta\Phi_i$ versus i was used to obtain the energy of germ formation $\Delta\Phi_g = (\Delta\Phi_i)_{\max}$. By identifying $\Delta\Phi_g$ in

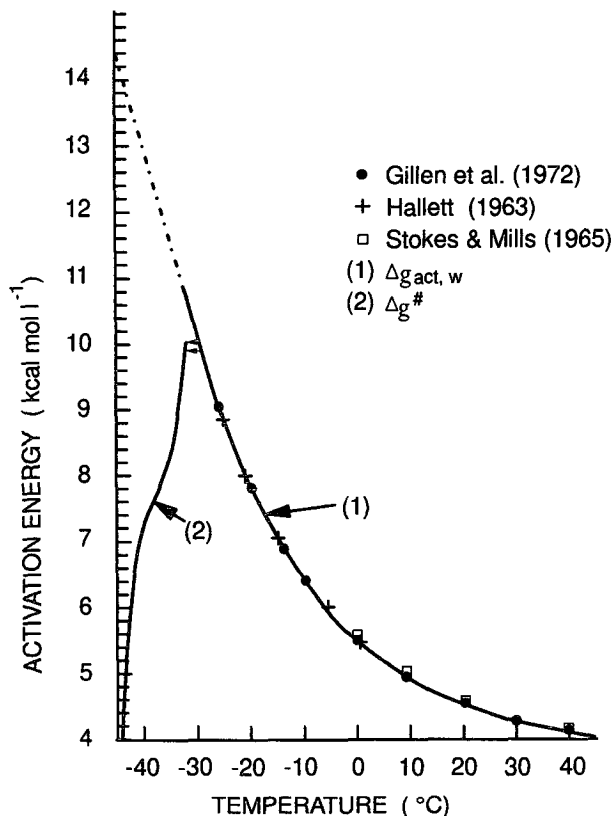


FIG. 11. Variation with temperature of the activation energy $(\Delta g)_{\text{act},w}$ for viscous flow and self-diffusion of water derived from viscosity and self-diffusion data and extrapolated to -45°C , and of the activation energy Δg^\ddagger for transfer of water molecules across the ice-water interface, obtained from Eq. (3) and listed in Table 1.

Eadie's model with ΔF_g in Eq. (3) we may compare the J values derived from the molecular model with those derived from the classical model. This comparison is

TABLE 2. Activation energy for transfer of water molecules across the ice-water interface.

Temperature (°C)	Δg^\ddagger (kcal mol ⁻¹)
-29	10.00
-30	10.00
-31	10.00
-32	9.60
-33	9.20
-34	8.60
-35	7.90
-36	7.75
-37	7.65
-38	7.45
-40	7.25
-41	6.85
-42	6.00
-43	5.15
-44	4.45

shown in Fig. 3. We notice excellent agreement between both models for supercoolings between 33° and 43°C. Unfortunately this agreement is purely accidental. A careful inspection of Eadies molecular model shows that his computation of J was based on a computation of $\Delta\Phi_g$ using Eq. (8), while the activation energy Δg^\ddagger for transfer of molecules across the water-ice boundary was estimated from values given by Dufour and Defay (1963), which, in turn, were based on Dorsey's (1940) data of the activation energy for viscous flow. These data provided values for Δg^\ddagger that were significantly lower than the values given in Fig. 11. At the same time Eadies molecular model significantly overestimated at low temperatures the interface energy $\sigma_{i,w}$ as compared to the $\sigma_{i,w}$ values given in Fig. 10, implying an overestimate of $\Delta\Phi_g$. These two errors must have compensated each other leading to the J values plotted. The agreement between the J values of the classical and of the molecular model can therefore not be used to further substantiate the Δg^\ddagger values derived by us from nucleation experiments via the classical model.

6. Conclusions

From this study the following conclusions may be drawn.

1) An analysis of recent thermodynamic data that characterize the physical state of supercooled water supports the suggestion of Angell (1982) that supercooled water exhibits a singularity at -45°C and it supports the conclusions of Binder (1984) that the free energy barrier to nucleation behaves similarly to other thermodynamic functions. This singularity is a result of the cooperative nature of the hydrogen bond between water molecules that becomes increasingly pronounced as the temperature decreases below 0°C .

2) The behavior mentioned in conclusion 1 results in a pronounced decrease with decreasing temperature of the density of water, the latent heat of freezing, and the interface energy between water and ice, and it causes a pronounced increase with decreasing temperature of the specific heat of water, the latent heat of evaporation, the viscosity, and the surface tension of water as well as of the activation energy for viscous flow and self-diffusion in water.

3) The rates for homogeneous ice nucleation in supercooled water derived from field observations at the cirrus cloud level and from recent cloud chamber studies are shown to be in quantitative agreement with the laboratory-derived lowest temperature to which ultra-pure drops of given size may be supercooled. Using these verified nucleation rates together with the recent physical properties data for supercooled water, the activation energy for the transfer of water molecules across the ice-water interface was computed using the classical nucleation equation. Below -30°C , the values thus computed were found to decrease with decreasing

temperature, in agreement with the expectation from the expansion cloud chamber data of Hagen et al. (1981) and with present knowledge on the structure of supercooled water.

4) Result 3 is in agreement with the notion that with decreasing temperature the freezing process becomes an increasingly cooperative phenomenon involving increasingly larger clusters of water molecules to transfer across the ice-water interface by breaking hydrogen bonds only at the cluster periphery.

5) The present results eliminate the earlier discrepancies that existed between the results of the classical nucleation equations, the field and laboratory data, and the results from the molecular model of Eadie (1971).

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