

SOME PECULIARITIES OF FREEZING OF METASTABLE WATER, INFLUENCING CLOUD ICE DEVELOPMENT

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1. INTRODUCTION

In the present-day knowledge of ice-forming microphysical processes in cold clouds, elements of uncertainty remain as yet. It becomes more and more clear that to understand physical mechanisms of formation of the disperse structure of cloud ice, special physicochemical properties of liquid water associated with its phase states and transitions must be investigated and taken into account. At the same time, to-day possibilities of experimental studying of fine details of these properties are essentially bounded.

Some important peculiarities of the frontal mechanism of freezing (crystallization) of metastable liquid water, supercooled ordinary water and A-water, are here considered basing on established features of interior intermolecular structure of different phase states of water as well as on some empirical facts associated with the freezing process. Specific factors of the impact of cloud droplet freezing process on the formation of parameters of ice disperse phase are discussed.

2. ON A TIME HISTORY OF CLOUD GLACIATION

The measurements performed in stratiform clouds with the cloud microphysical aircraft instrumentation of the Central Aerological Observatory revealed that a fine-dispersed ice fraction with particle sizes smaller than 20 μm is already present in clouds traditionally regarded as pure water ones (Nevzorov, Shugaev, 1992a, 1992b). The concentrations of ice particles in these clouds are comparable with the concentrations of their droplets

and, on the whole, by several orders of magnitude exceed the known concentrations of ice-forming nuclei. Their long-time coexistence with the liquid water ($\rho = 1 \text{ g}\cdot\text{cm}^{-3}$) disperse phase can be explained in terms of very slow mass exchange by molecular diffusion in quiet (relative to a particle) air. In this connection, the question arises about a role of droplet freezing in cloud glaciation process.

As is known, the water freezing nuclei (FN) form the overwhelming part of natural ice-forming nuclei; hence their mean concentration should closely follow the Fletcher's empirical formula for the concentration of ice-forming nuclei against the cloud temperature. However, the cloud droplets freeze on these nuclei far not simultaneously. The time dependence of concentration of freezing droplets can be estimated with taking into consideration the increase of the freezing probability, i.e. of concentration N_{FN} of active FN, along with droplet sizes. The mean concentration of FN active at given temperature, T , and droplet diameter, a , has been deduced (Nevzorov, 2006a) using Bigg's experimental data on their dependence on droplet size (Franks, 1985):

$$N_{FN}(T, a) = N_0 \cdot (a/a_0)^{1.7} \exp(-0,6T), \quad (1)$$

where N_0 and a_0 are for $T = 0^\circ\text{C}$. For simplified model of monodisperse droplet cloud in the developmental stage ($da/dt > 0$), the rate of droplet freezing per a unit volume will follow the expression:

$$N'_{FT} = \frac{\partial N_{FN}}{\partial a} \frac{da}{dt} = 1,7N_0 \frac{a^{0,7}}{a_0^{1,7}} \frac{da}{dt} \exp(-0,6T). \quad (2)$$

In the process, ice crystals grow faster than water droplets owing to higher supersaturation relative to them. With time, the value of da/dt comes to zero and remaining droplets begin evaporating without freezing inasmuch as their active FN are spent. As might seem, the added ice portion proves too little to make appreciable contribution to the existing ice fraction and especially to its evolution. However the latter is not so; as will be shown further, a factor accompanies the droplet freezing process that promotes acceleration of ice particle growth in formation of their size spectra.

3. UNIQUE PROPERTIES OF LIQUID WATER AT $T < 0^\circ\text{C}$

A number of special properties of water at negative temperatures are caused by the participation of intermolecular hydrogen bonds (HB) in organization of its internal structure. As against a rigid spatial lattice in crystalline ice, in ordinary liquid water (with density $\sim 1 \text{ g}\cdot\text{cm}^{-3}$), named here water-1, HB are partly disrupt chaotically in space and time. The higher density of the water-1 specifies that HB hold larger distance between molecules than usual oscillatory bonds (an effect hereinafter called repulsive effect of HB). Even much higher density, somewhat more than $2 \text{ g}\cdot\text{cm}^{-3}$ (Delsemme, Wenger, 1970; Nevzorov, 2006b), belongs to amorphous water deprived of HB at all to all attributes.

The specific concentration of HB in water-1 experiences an inverse relation with the energy of thermal vibrations of molecules. As a result, with the temperature rising, the water-1 density ρ_w should decrease due to an increase of the amplitude of thermal vibrations of molecules; at the same time, ρ_w should increase due to a decrease of HB concentration. The known maximum of ρ_w value at 4°C is caused by the prevalence of the former tendency at higher temperatures and of the latter one at lower temperatures.

The experimental dependence $\rho_w(T)$ for water-1 in the range from 0°C to -34°C reveals a progressive decrease of its density

when the temperature lowers (Franks, 1985). This dependence is shown in Figure 1 for the difference between of the density of liquid water and ice, $\Delta\rho = \rho_w - \rho_i$ where $\rho_i = 0,917 \text{ g}\cdot\text{cm}^{-3}$, with its extrapolation to the region of lower temperatures, based on the following considerations. The decrease of the water-1 density means that its structure approach to crystalline ice in the specific concentration of HB and therefore in the relative total volume of instant ice-like clusters. Hence the probability increases of the stochastic formation of homogeneous ice nuclei with a zero threshold of nucleation energy. At a critical temperature of water-1 existence, defined as a temperature of its wholly homogeneous freezing and equal to -39°C (Franks, 1985), the water-1 comes up with crystalline ice in density. In turn, the equality of their densities means in principle that the internal energy of water-1 becomes equal to the internal energy of ice at -39°C , and the latent energy of its freezing vanishes.

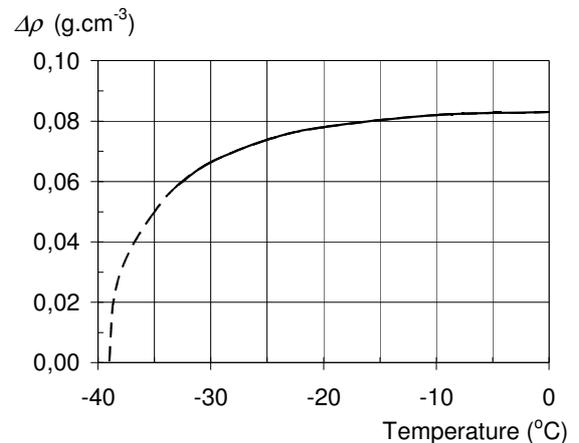


Fig.1. The temperature dependence of the difference between the densities of liquid water-1 and ice I. The solid curve is by (Franks, 1985); the dashed segment is an extrapolation.

Assuming that as a first approximation, the $L_f(T)$ value is proportional to the difference $\rho_w(T) - \rho_i$, the proportionality factor $L_0 \approx 316 \text{ J}\cdot\text{g}^{-1}$ is chosen so that the corresponding relation

$$L_f(T) = L_0 \frac{\rho_w(T) - \rho_i}{\rho_w(0) - \rho_i} \quad (3)$$

to be as possible close to the reference dependence at $T > -30^\circ\text{C}$. The ice density is assumed to be temperature-independent. Figure 2 shows the dependence (3) in comparison with the reference curve $L_f(T)$ (e.g. Mazin, Khrgian, 1989).

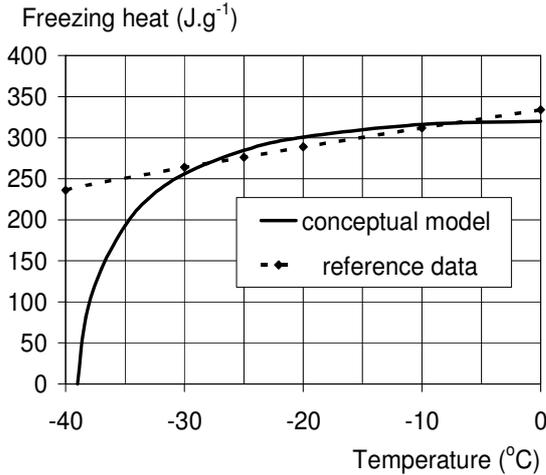


Fig. 2. Conceptual and reference models of the temperature dependence of the specific latent energy of water-1 freezing.

In turn, A-water, as being deprived HB (Nevzorov, 2006b), has not the specified temperature dependences of its properties and behaves as a usual simple liquid.

4. PARADOXES AND PECULIARITIES OF FRONTAL FREEZING MECHANISM

Both the metastable liquid phases of water, ordinary water-1 and amorphous A-water, when freezing (crystallizing) transform into the same phase, ice I with the density $\sim 0.92 \text{ g}\cdot\text{cm}^{-3}$. The first-order phase transition takes place in the both cases, which requires the discrete separation of the phase spaces by reason of the absence of intermediate state. The process of freezing of a continual water volume consists in propagation of the phase interface, or the freezing front, in the liquid

medium from the nucleation center, leaving behind a continuous medium of crystalline ice.

With different densities of substances before and behind the freezing front, especially in the case of A-water, a freezing droplet should apparently change its shape or be destroyed by the internal stress. In fact, a lot of observations and experiments demonstrate that the frozen water droplets of various sizes remain spherical. For A-water, this is pronounced in spherical shape of frozen droplets in a pattern of crystals riming in ICC (Pruppacher, Klett, 1978). The assumptions on the initial formation of an ice crust on the droplet surface or on plicated surface of the freezing front (Franks, 1985) appear devoid of physical basis.

Another apparent paradox of the frontal freezing mechanism follows from the conventional statement that the latent energy of the phase transition is released in purely thermal form. If the heat is released immediately during ice phase formation, just formed ice should be subjected to the initial temperature increment

$$\Delta T_0 = \frac{L_f}{c_{pi}}, \quad (4)$$

where $c_{pi} \approx 2,0 \text{ J}\cdot\text{g}^{-1} \text{ K}^{-1}$ is the specific heat capacity of ice. For water-1 at temperatures between -35°C and 0°C , taking L_f according to (4), the ΔT_0 values are from 100K to 160K.

More impressive result is demonstrated by A-water, for which $L_f = L_i - L_e \approx 2300 \text{ J}\cdot\text{g}^{-1}$, where L_i is the evaporation heat of ice; here (4) yields $\Delta T_0 = 1150 \text{ K}$. Thus, at the instant of its formation and during a finite time of temperature relaxation, just formed ice should be at the temperature being much higher than its melting temperature, which in principle rules out the possibility of its existence. As far as we know, this paradox inherent namely to the frontal freezing has yet no physically founded explanation.

Within the current knowledge of the intermolecular structure of various water phases, both paradoxes meet the same explanation (Nevzorov, 2006a).

The continuous motion of the interphase surface is caused by the consecutive attachment of molecules of liquid to the ice lattice. The retained and newly formed HB serve as connecting links between both phases, providing their continuous cohesion. This excludes any possibility of tangential slip of a liquid layer adjacent to the frontal surface. For this reason and due to its internal viscosity, the liquid trapped by the moving front is not deformed with respect to the base of solid ice with the result that the newly formed ice phase retains the initial volume of the liquid phase. However, since the ice density is smaller than the liquid one, an excess in mass of liquid water with respect to ice occurs at the freezing front and is thereby rejected in the form of unbound molecules. The energy released at the front is transferred to these liberated molecules, converting into their kinetic energy.

If these molecules remain in the liquid medium they would totally transfer to it both their mass and energy. At that, the mass excess would distort the initially spherical shape of a frozen droplet. As for the energy, it is known that supercooled water can immediately freeze at temperatures arbitrarily close to 0°C, which implies that the molecules rejected from the freezing front leave the liquid with carrying away all the gained energy. Thus the freezing process remains isothermal in itself, except produced by its molecular flow carrying away all released energy and equivalent to hot vapor.

That these unbound molecules leave the condensed medium through the liquid space can be certified by a behavior of water freezing in a vessel which low part, being the closed volume for liquid, is subjected to deformation or destruction under the internal pressure, rather than the part of ice formation. Using an analogy with quite (film) boiling, the flow of free molecules in liquid can be likened to molecular vapor outflow from a hot surface. Details of this phenomenon, still poorly studied, possibly include a chain energy transfer from molecule to molecule.

As an indirect experimental confirmation of the stated vapor outflow from freezing water,

occurrence of "an unidentified gas" (Franks, 1985) in the process can serve.

It follows from all above that the water portion transforming into outside vapor during the freezing is

$$m_v/m_w = (\rho_w - \rho_i)/\rho_w, \quad (5)$$

where m_w and m_v are the liquid and vapor masses, respectively. For water-1, assuming the dependence $\rho_w(T)$ by Fig.1, this fraction is 8.3% at -1°C , 5.2% at -35°C , and rapidly vanishes when the temperature tends to -39°C . In freezing of A-water with the density of $\sim 2.1 \text{ g}\cdot\text{cm}^{-3}$, approximately 56% of its mass transforms into vapor independently of temperature. According to estimations (Nevzorov, 2006a), in both cases effective velocity of molecules while crossing the liquid-to-air interface is 60 to 80 $\text{m}\cdot\text{s}^{-1}$.

The considered peculiarities of supercooled water freezing mechanism offer a simple alternative explanation of two-stage effect of droplet freezing (Pruppacher, Klett, 1978). The first stage is the isothermal freezing properly, and the second one is the result of condensation of ice supersaturated vapor (including just liberated) on the ice replacing water.

5. MICRO TURBULENCE EFFECT

In the process of freezing of a droplet suspended in air, the motion of water molecules emitted by this droplet is transferred to the surrounding air, thereby causing its forced outflow from the droplet surface and the appearance of compensating eddy motions. As a result, a zone of microscopic (comparable with cloud particle sizes) scale turbulence develops around the droplet. In the light of cloud microstructure evolution, the influence of these disturbances on the rate of growth or evaporation of cloud particles through the mechanism of convective diffusion of water vapor is of interest to us.

Let the zone of disturbances generated by the freezing of an individual droplet with the diameter a occupy a certain effective volume

V. Under the assumption that the time of dissipation of the disturbance energy is much greater than the time of complete freezing of the droplet, the initial turbulent energy, $E_0(a)$, of the disturbance zone can be expressed both in terms of the turbulent kinetic energy of air particles and in terms of the total kinetic energy of liberated molecules directly at their outlet from the droplet:

$$E_0(a) = V\rho_a \frac{\Delta u_a^2}{2} = \frac{\pi}{6} a^3 (\rho_w - \rho_i) \frac{u_{m2}^2}{2}, \quad (6)$$

whence

$$V = \frac{\pi}{6} a^3 \frac{\rho_w - \rho_i}{\rho_a} \frac{u_{m2}^2}{\Delta u_a^2}. \quad (7)$$

Here, ρ_a is the air density; u_{m2} and Δu_a are the rms velocities of the molecules and of air pulsations, respectively. Since the velocities of turbulent motions decrease with distance from the droplet increasing, then, as follows from (7), the determination of the disturbance-zone scale depends on the choice of an effective value of Δu_a to answer a required criterion.

Let a crystal with the effective size b , large enough to retain its rest inertia, be located within such disturbance volume. Following and taking into account the anisotropy of turbulent air blow-off, we will assume the inequality

$$\text{Re}_b = \frac{b \cdot \Delta u_a}{\mu} > 1 \quad (8)$$

(where μ is the kinematic viscosity of air) as a tentative criterion of accelerated convective-diffusion mode of particle growth. It follows from (7) and (8) that the "active" volume V increases with increasing sizes of both the freezing droplet and the particle falling into its disturbance zone. In real clouds, the probability as estimated of this event is rather low compared to unity but increases with the particle size. Hence in the process of collective freezing of droplets a small fraction of cloud

particles will experience a progressive acceleration of growth; i.e., the right-hand wing of ice particle size spectrum will increase most rapidly.

Upon the completion of the freezing process of a droplet, the excited turbulent energy attenuates rapidly, thereby converting into heat energy. Owing to the acquired buoyancy, the heated volume of air around the frozen droplet arises. In the process of the cloud glaciation, these scattered zones of buoyancy form spatiotemporal inhomogeneities, or turbulent pulsations of the resulting updraft. Such "secondary" microturbulence additionally accelerates the mass exchange process in a cloud.

The irreversible microscale turbulence is settled in the cloud when the particles of ice and accompanying A-water reach sufficient sizes for the gravitational fall causing appreciable adjacent vortex. The phase transformation of a cloud is concluded with its avalanche transition into mixed state with A-water serving as its liquid disperse phase.

6. CONCLUSION

In the process of development of a water cloud, the freezing of its droplets occurs not at once but is lasting in time owing to increase in probability of freezing of droplets of ordinary water and A-water with their rising. An important specific feature of the frontal mechanism of freezing of an individual droplet is that during freezing, the droplet emits molecular vapor carrying the released energy of the phase transition. As a result, a zone of short-living microscale turbulence arises around each freezing droplet. The ice crystal which falls into this zone experiences much more rapid growth in convective diffusion mode than in molecular diffusion one. Such chance for the acceleration of growth of an individual crystal occurs with very small probability but rising with the crystal becoming larger. By this reason, ice crystals grow far not equally and only their little part reach precipitation sizes. With sufficient collective enlargement of crystals, their gravitational sedimentation becomes a source of the ir-

revocable microscale turbulence, which results in convective diffusion mode of the Bergeron mass exchange. The phase transformation of a cloud is concluded with its avalanche transition into the mixed state, where A-water becomes the only liquid disperse phase.

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