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Internal Mechanism of Metastable Liquid Water Crystallization and Its Effects on Intracloud Processes

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Abstract—Specific features of an internal freezing (crystallization) mechanism for both ordinary supercooled water and amorphous water (A-water) are considered. Amorphous water plays the role of an intermediate phase in condensation ice formation and is capable of metastable existence in the form of cloud drops. It is demonstrated that, after passing the crystallization front, the ice phase takes the liquid-phase volume and the excessive water mass is detached from the front in the form of free molecules, which escape through the liquid into the gaseous medium. The released energy of the phase transition is removed with these molecules, so that the formed ice retains the initial temperature of the liquid. A high-rate vapor outflow from the freezing drop generates (around the drop) a zone of microscale turbulence, which accelerates the mass exchange between cloud particle and vapor. Since the freezing frequency of drops in a cloud increases with their size, the effects of their freezing develop initially in time. At the same time, these effects initiate such processes that end in a complete evaporation of supercooled water drops and in a sharp enlargement of A-water and ice particles, i.e., in cloud transition to such a phase-mixed state where the liquid disperse phase consists of A-water drops. A reduction in the duration of the initial (fine-dispersed) stage of the evolution of clouds with their temperature lowering can be explained only by the development of microscale disturbances as a result of the freezing of drops.

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1. INTRODUCTION

Many uncertainties and contradictions remain in the present-day concepts of microphysical processes in clouds with temperatures below 0°C, or cold clouds. As has been shown in recent works [1–4], the majority of these concepts originate from insufficient knowledge of the physicochemical properties of water associated with its structural polymorphism and phase transitions. Investigations in this field [5, 6] have not yet reached the level of systematic generalizations suitable for widespread use. Investigations of the liquid states of water, metastable in relation to the transformation to crystalline ice, are particularly difficult. Apart from supercooled ordinary water with the density 1 g cm^{-3} (henceforth referred to as water-1), amorphous water (A-water) with the density 2.1 g cm^{-3} has such a state [2]. The amorphous water forms the liquid disperse phase of mixed clouds, which is in the condensation equilibrium with ice [2, 3]. Both of the liquid modifications of water are produced by condensation and survive in clouds until the conditions for their evaporation or freezing (crystallization) are formed.

The approaches existing in the physics of cold clouds take into account such explicit effects of the freezing of supercooled water droplets as the generation of disperse crystalline ice, air heating by the released heat, and the supersaturation of the background humidity over the ice particles being formed. Meanwhile, the very process of water freezing involves phenomena that cannot be explained within the framework of traditional concepts [5, 7] and thereby point to the existence of still unknown details in the mechanism of freezing.

This study proposes a physical model for the internal mechanism of water freezing and its effects on the processes proceeding in atmospheric clouds. The proposed model is based on modern knowledge of the structures of different phase states of H_2O and leans upon classical laws of physics and upon well-known phenomena. A concrete problem of the phase evolution of cold clouds, which is solved on the basis of the proposed model, is considered.

2. PARADOXES ASSOCIATED WITH THE FREEZING OF WATER

Both of the metastable liquid phases of water (water-1 and A-water) change during their freezing (crystallization) to the same phase—ice I with the density ~0.92 g cm^{-3}. The first-order phase transition takes place in both of the cases. As is known [5, 6], such a transition means a jumplike separation of the phase spaces by reason of the absence of intermediate states. The process of freezing of a continual water volume is as follows. The phase interface or the crystallization front propagates in the liquid medium from the nucleation center and leaves behind it a continuous medium of monocrystalline ice. The paradoxes of metastable-water freezing, which remain unsolved, are related to this frontal mechanism.

The first paradox is associated with the axiomatic concept of the conservation of mass of freezing water at the crystallization front (along with recognition of the integral effect of evaporation) [5]. If this condition is fulfilled, the difference between the phase densities on both sides of the front must result in the deformation of the freezing particle, i.e., in the distortion of the initial spherical shape of the droplet to the point of its destruction [8]. Actually, as numerous experiments indicate, the frozen water droplets of different sizes invariably retain a spherical shape. For A-water, this effect is expressed, for example, in the pattern of cloud crystal riming by settled and then frozen droplets [9]. The existing hypotheses that an ice crust is initially formed on the droplet surface or that the freezing front has a folded surface [5] are unfounded physically and are beneath the simplest criticism.

The second paradox stems from the universal concept that the latent energy of the above phase transition is released as pure heat. According to elementary considerations, the heat energy must release exactly at the moments of phase restructuring, i.e., immediately at the front of ice-phase formation. In this case, as soon as the ice is formed, its temperature must increase instantaneously by

$$\Delta T_0 = \frac{L_\mathrm{f}}{c_{p\mathrm{i}}}, \tag{1}$$

where $c_{p\mathrm{i}} \approx 2.0$ J g^{-1} K^{-1} is the specific heat of ice and L_f is the specific latent heat of water freezing. From the tabulated data for water [10], we have $L_\mathrm{f} = 236$ J g^{-1} at –40°C and $L_\mathrm{f} = 334$ J g^{-1} at 0°C. The corresponding values of ΔT_0 are about 120 and 170 K, respectively. Thus, at the moment of its formation and during the initial period of temperature relaxation, the temperature of ice must substantially exceed its melting point, thereby physically eliminating the possibility of ice existence.

The calculation for A-water yields a still more dramatic result. According to the experimental estimation [1–3], for this water, the heat of evaporation at –30°C is $L_\mathrm{e} \approx 550$ J g^{-1}; consequently, $L_\mathrm{f} = L_\mathrm{i} - L_\mathrm{e} \approx 2300$ J g^{-1}, where L_i is the heat of evaporation of ice. Expression (1) yields $\Delta T_0 \approx 1150$ K.

The latter paradox is most frequently disregarded in the literature. Some attempts to explain this paradox are reduced to the general idea that the processes at the crystallization front are of a more complicated character than follows from the above elementary considerations.

The impossibility to explain the aforementioned paradoxes from the standpoint of the existing fundamental concepts suggests that these paradoxes are not the consequences but the initial properties of the mechanism of frontal crystallization of metastable water. Namely:

(i) The water volume in the form of ice rather than the water mass is preserved during the passage of the crystallization front.

(ii) The latent energy of crystallization is released partially or completely in a form other than pure heat.

The physical feasibility of the above properties is substantiated in the following section.

3. MICROPHYSICS OF WATER FREEZING

The difference between the internal structures of liquid water and crystalline ice underlies the microprocesses accompanying frontal crystallization. The structure of ice I is formed by a regular spatial lattice of intermolecular hydrogen bonds. The structure of water-1 is a similar but "unfinished" lattice in which a part of the bonds are broken chaotically in space and time [7]. Amorphous water is altogether free of ordered hydrogen bonds and, in this sense, is a simple liquid.

Note that, with an increase in the specific concentration of hydrogen bonds (as in the water-1–crystalline ice transition), the density of the water condensate decreases. This finding means that the hydrogen bond does not bring together but, in contrast, brings the molecules encompassed by it away from one another as compared to oscillatory bonds inherent in simple liquids.

A continuous advance of the phase interface in the process of crystallization is caused by the consecutive attachment of molecules from the liquid to the crystal lattice of ice. Retained and newly formed hydrogen bonds serve as coupling links between both phases, ensuring their constant cohesion. This cohesion eliminates the possibility of slipping along the frontal surface of the liquid layer adjacent to it. For this reason and owing to its internal viscosity, the liquid captured by the moving front does not experience any deformation with respect to the solid ice base. As a result, after the front passage, the ice phase takes the initial geometric shape and volume of the liquid phase. A decrease in the mass of this volume because of a lower ice density means a decrease in the volume concentration of molecules (an analogue of the density); the only cause for this decrease can be due to the release of molecules excessive with respect to the ice structure and unrelated to it. The energy released at the crystallization front is directly transferred to these molecules, while being converted into their kinetic energy.

How do these free molecules leave the condensed medium? Unfortunately, the available knowledge cannot provide a well-founded answer to this question. The known experiment of a gradual water-freezing process extending downward in a vessel can somewhat clarify this question. It can be noted that, during such freezing, the deformation or destruction under the action of internal pressure is predominantly experienced by the lower part of the vessel filled with unfrozen water rather than by the main zone of ice formation. This result must imply that the forming ice not only retains the initial volume of liquid water but also is impermeable for the escape of excessive molecules formed by the freezing front. The pressure in the closed volume of liquid increases owing to the supply of new molecules into it. Hence, it follows that the molecules detached by the freezing front can escape into the ambient air only through an intermediate liquid medium.

By analogy with the process of quiet (film) boiling, the outflow through the liquid of free molecules detached from the crystallization front can be compared to a molecular flow from a hot surface contacting with the liquid. The details of this phenomenon have been poorly understood up to now and appear to include a chainlike energy transfer from molecule to molecule. It is known that the freezing of supercooled water droplets can occur at temperatures arbitrarily close to 0°C. This is equivalent to the phenomenon when all molecules detached from the front leave the droplet without transferring at least a noticeable fraction of their energy to it.

Let us isolate a small liquid-phase volume Δv, containing the mass $\Delta v\rho_w$, where ρ_w is the liquid density. After the passage of the crystallization front, the part of this mass $\Delta v\rho_i$, where ρ_i is the ice density, remains in the given volume as the ice phase and the remaining part of this mass $\Delta v(\rho_w - \rho_i)$ is removed with the molecular-vapor phase being formed. The energy balance equation for the given volume has the form

$$L_f\rho_i = \frac{u_{m2}^2}{2}(\rho_w - \rho_i), \qquad (2)$$

where u_{m2} is the rms velocity of motion of free molecules.

Let us consider the temperature dependences of the quantities appearing in (2). The data on the dependence $\rho_w(T)$ for supercooled water-1 are borrowed from the curve obtained experimentally for $T > -34$°C and presented in [5]. The continuation of this curve into the region of lower temperatures is constructed in Fig. 1 from the following considerations. The density of water-1 decreases with temperature lowering because of an increase in the specific concentration of hydrogen bonds, a phenomenon that means that the structure of water-1 approaches the structure of crystalline ice. In this case, the probability of stochastic formation of homogeneous ice nuclei with a zero energy threshold of nucleation increases. At the limiting temperature of water-1 existence, which is defined as the temperature of its homogeneous freezing and is equal to –39°C under normal conditions [5], the density and internal energy of water-1 must become equal to the density of ice and the internal energy of ice, respectively. Consequently, at –39°C, the latent energy of its freezing must vanish.

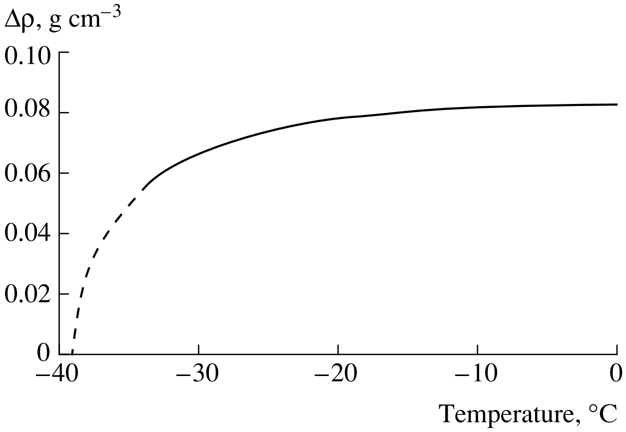

Fig. 1. Temperature dependence of the difference between the densities of liquid water-1 and ice I. The density of ice I is assumed to be 0.917 g cm^{-3}. The continuous segment is constructed from the data of [5]; the dashed segment is an extrapolation.

The latter circumstance is not reflected in the reference values of the latent freezing heat $L_f(T)$ as a function of the temperature [10]. These values are derived from a linear approximation of experimental data if $T > -30$°C and from its extrapolation for lower temperatures. As an approximate alternative model, we will assume that the quantity $L_f(T)$ is proportional to the difference $\rho_w(T) - \rho_i$. We will select the proportionality coefficient in such a way that the relation obtained be maximally close to the reference dependence for $T > -30$°C:

$$L_f(T) = L_0\frac{\rho_w(T) - \rho_i}{\rho_{w0} - \rho_i}, \qquad (3)$$

where $L_0 \approx 316$ J g^{-1} and $\rho_{w0} = 1$ g cm^{-3}. The ice density ρ_i is assumed to be temperature-independent. In Fig. 2, dependence (3) is compared to the reference plot of $L_f(T)$. The calculated temperature dependences of other properties of water-1, including the mass fraction transformed into vapor during the freezing, are illustrated by the values presented in the table.

As for A-water with the density $\rho_A \approx 2.1$ g cm^{-3}, the part of its mass equal to $(\rho_A - \rho_i)/\rho_A$ is transformed into vapor at the crystallization front. In this case, the quantity L_f must not depend significantly on temperature, because the type and specific concentration of intermolecular bonds in an amorphous liquid are invariant.

The laboratory experiments with low-temperature amorphous water described in [5, 6, 12] can serve as

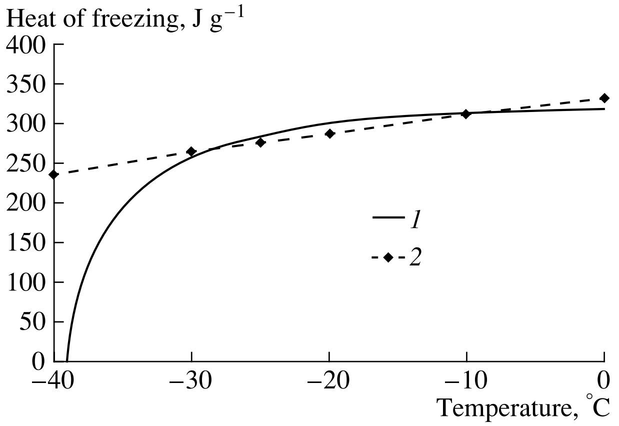

Fig. 2. Conceptual (*1*) and reference (*2*) models of the temperature dependence of the specific latent energy of water-1 freezing.

support for our inferences. It was found in some experiments that the condensate virtually retains its volume after its transition to ice I, a finding that led to the concept of "light" amorphous water, whose density is close to the density of crystalline ice. In other cases, a noticeable and ambiguous increase in the volume was observed, which suggested a "high-density" modification of amorphous water [12]. All such density values are strongly underestimated compared to the results obtained by other methods and close to one another [1, 2, 13]. In our opinion, this underestimation is a consequence of the aforementioned loss of a part of the mass of metastable condensate during its crystallization, while substantial scatter in the estimates is caused by the secondary condensation of released vapor, whose efficiency depends on experimental conditions. A substantial, from a few tenths to tens of degrees, scatter in the temperature increase of the condensate in the process of its crystallization confirms the effect of secondary condensation.

Properties of supercooled water-1

Temperature, °C	Density, g cm^{-3}	Latent energy of freezing, J g^{-1}	Fraction evaporated during freezing $(\rho_w-\rho_i)/\rho_w$
0	1.00	316	0.083
–10	0.999	312	0.082
–20	0.995	297	0.078
–30	0.983	264	0.068
–35	0.967	251	0.052
–39	0.917	0	0

Both the direct weighing of the condensate sample before and after crystallization and the monitoring of the accompanying change in the environmental water vapor concentration could objectively verify all of the versions presented here. To our knowledge, such experiments have not been conducted purposely; however, the release of an unknown gas was noted [5]. Supposedly, this gas is precisely water vapor.

4. DYNAMIC EFFECT OF THE FREEZING OF DROPLETS

It follows from (2) and (3) that, within the framework of the proposed concept, the outflow rate of freed molecules during water-1 freezing is unrelated or at least weakly related to the temperature and is

$$u_{m2} = \sqrt{\frac{2L_0\rho_i}{\rho_{w0}-\rho_i}} \approx 84\ \mathrm{m\ s^{-1}}. \qquad (4)$$

For A-water, relation (4) yields the value $u_{m2} \approx 60\ \mathrm{m\ s^{-1}}$.

In the process of freezing of a droplet suspended in air, the motion of 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 microscale 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 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 molecules freed directly at their outlet from the droplet:

$$E_0(a) = V\rho_a\frac{\Delta u_a^2}{2} = \frac{\pi}{6}a^3(\rho_w-\rho_i)\frac{u_{m2}^2}{2}, \qquad (5)$$

whence

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

Here, ρ_a is the air density and Δu_a is the rms velocity of air pulsations in the zone of disturbance. Since the velocities of turbulent motions decrease with increasing distance from the droplet, then, as follows from (6), the determination of the disturbance-zone scale depends on the choice of the effective value of Δu_{a} meeting some or other criterion.

Let a crystalline particle with the equivalent diameter b, whose mass allows it to retain the inertia of rest, be located in the field of such disturbances. Using the conclusions made in [11] about the influence of blowing-off of the droplet on its growth rate and taking into account the anisotropy of turbulent blowing-off, we will assume the inequality

$$\mathrm{Re}_b = \frac{b\Delta u_{\mathrm{a}}}{\mu} > 1, \qquad (7)$$

where μ is the kinematic viscosity of air, as a tentative (qualitative) criterion of the convective-diffusion regime of particle growth. It follows from (6) and (7) that the "active" volume V increases with increasing size of both the freezing particle and the particle located in the field of disturbances of the former. In real clouds, according to estimations, the probability that a particle with the corresponding size will fall into the effective volume is rather low compared to unity, and this probability, all other factors being equal, increases with the particle size. Owing to this phenomenon, in the process of mass freezing of droplets, a small fraction of cloud particles will experience a progressive acceleration of growth; i.e., in the particle size spectrum, the length of its right-hand wing will increase most rapidly.

Upon the completion of the droplet freezing process, turbulent motions attenuate rapidly, thereby converting into heat energy. Owing to the acquired buoyancy, the heated volume of air around the frozen droplet rises. In the process of collective freezing in a cloud, these scattered zones of buoyancy form spatiotemporal inhomogeneities or turbulent pulsations of the resulting rising motion. Such a "secondary" microturbulence undoubtedly enhances the effect of an accelerated growth of individual droplets.

5. APPLICATION IN THE PHYSICS OF COLD CLOUDS

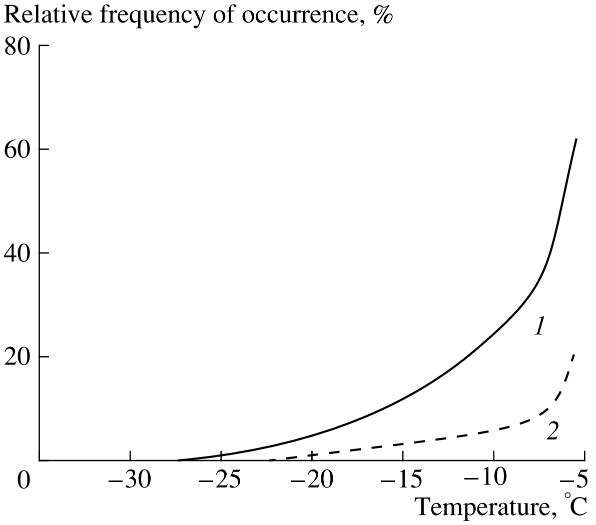

Fig. 3. Experimental temperature dependence of the relative frequency of occurrence of stratiform clouds with a latent-mixed structure: (*1*) detected and (*2*) suggested (because of an uncertain identification). The upper curve demonstrates the total frequency of occurrence (according to the data of [15]).

Measurements performed in stratiform clouds with the cloud microphysical aircraft instrumentation (SOMK) of the Central Aerological Observatory [14] revealed the presence of a fine-dispersed ice fraction with a particle size smaller than 20 μm in the majority of clouds, traditionally regarded as pure water clouds [14, 15]. The concentrations of ice particles in these clouds are comparable with the concentrations of droplets in them and, on the whole, exceed the known concentrations of ice-forming nuclei by several orders of magnitude. Such a cloud structure is called "latent-mixed," because the ice fraction is hidden from standard observations. The presence of disperse ice in a cloud was not always detectable, even with the more sensitive SOMK facilities (Fig. 3). There is good reason to conclude that ice particles appear in a cloud at the earliest stage of its development and are able to survive in it during many hours, as follows from the observed stability of water clouds. Such a longevity of an unstable latent-mixed state of stratiform clouds points to a very slow growth of ice particles despite a substantial supersaturation of vapor over them. All particles grow or evaporate most slowly in the regime of molecular diffusion of vapor. Small sizes of these particles, ensuring negligible rates of their gravitational settling and a complete entrainment by air motions in the absence of turbulent motions with scales on the order of their sizes, are the necessary conditions for the aforementioned regime. As the sizes of ice crystals and droplets of A-water accompanying them grow, the rates of their gravitational settling increase. The blowing-off effect arising in this case in turn accelerates the growth of such particles, and microscale disturbances excited in the air by their fall favor the convective-diffusion mass exchange of the surrounding particles with vapor. When a certain fraction of particles reach the sizes sufficient for their rapid fall, a continuous and irreversible microscale turbulence is established in the cloud. Owing to intensification of the vapor outflow onto ice and A-water, the condensation growth of water-1 droplets slows down and then changes to their evaporation. This Bergeron process of phase recondensation is completed with the transition of a water cloud to a normal mixed state, in which ice crystals attain millimeter sizes and become easily detectable and A-water droplets replace the liquid disperse phase [2–4]. Thus, the duration of the latent-mixed state of the cold cloud is controlled by the maximum growth rate of ice and A-water particles.

According to observations [4, 10], the relative frequency of occurrence and, consequently, the mean lifetime of allegedly pure water clouds, i.e., actually, latent-mixed stratiform clouds, rather abruptly decrease with their temperature lowering as is shown in Fig. 3. At first glance, such a dependence seems regular because the probability of droplet freezing increases rapidly with decreasing air temperature [16]. However, an increase in the concentration of frozen droplets enhances the competition for the vapor outflow and, therefore, must lead to the slowing down of the growth rate of ice particles and to the limitation of their final sizes. A decrease in the absolute ice supersaturation of vapor and a decrease in the liquid component of the water content of clouds also favor these processes [4]. According to these considerations, as the temperature decreases, the cloud must indefinitely long retain its fine-dispersed mixed state, which can be regarded as the water state from the methodological point of view.

It remains to conclude that the actual decrease in the lifetime of the initial fine-dispersed structure at low temperatures is associated with the influence of microscale disturbances generated by frozen droplets on particle growth. Let us try to reveal such a relation with the aid of the theory describing the maximally simplified model of evolution for the microstructure of a cloud in its latent-mixed stage.

As is known, water-freezing nuclei form the overwhelming part of natural ice-forming nuclei. Therefore, the empirical formula derived by Fletcher for the mean concentration of ice-forming nuclei

$$N_{\mathrm{FN}}(T) = N_0 \exp(-0.6T), \tag{8}$$

where $N_0 \approx 10^{-8}$ cm^{-3} and T is the air temperature in °C, can serve as a generalization of the temperature dependence of their concentration in the atmospheric air.

To solve the formulated problem, it is necessary to consider the freezing of droplets in the course of time. The relation of the freezing probability of a droplet to its size a, which can be derived from the Bigg experimental dependence between the sizes of droplets and the temperatures of their freezing, can serve as a prerequisite for obtaining the sought-for solution. This dependence, graphically presented in [5], can be written analytically in the form $T - T_0 = 2.8\ln a/a_0$, where T_0 and a_0 are arbitrary initial conditions. Under the assumption that the same nuclei become active with increasing temperature and droplet size, the concentration of freezing nuclei as a function of the a/a_0 ratio can be found from the above Bigg dependence and formula (8). After some transformations at $T_0 = 0$°C, the generalized expression for the mean concentration of atmospheric freezing nuclei, active at the given temperature and droplet size, takes the form

$$N_{\mathrm{FN}}(T, a) = N_0 (a/a_0)^{1.7} \exp(-0.6T). \tag{9}$$

Here, a_0 is the diameter of the droplets (supposedly, not exceeding 2 μm) for which dependence (8) is determined from experimental conditions.

Let the inflow of water-1 supersaturating vapor occur in a latent-mixed cloud. Owing to this inflow droplets (and the more so, other particles) experience a continuous condensation growth. Assume for simplicity (which will not affect a general character of the conclusions) that all water-1 droplets are identical in size and growth rate. Then, the frequency of droplet freezing in a unit of volume of the cloud will be

$$\begin{aligned} N'_{\mathrm{FT}} &= \frac{\partial N_{\mathrm{FN}}(T, a)}{\partial a}\frac{da}{dt} \\ &= 1.7 N_0 \frac{a^{0.7}}{a_0^{1.7}}\frac{da}{dt}\exp(-0.6T). \end{aligned} \tag{10}$$

With allowance for the existence of two possible mechanisms of the particle–vapor mass exchange, in a general case, the well-known approximation for the growth rate of a droplet takes the form

$$\frac{da}{dt} = \frac{4}{a\rho_{\mathrm{w}}}(D_{\mathrm{m}} + D_{\mathrm{c}})\Delta C_v, \tag{11}$$

where D_{m} and D_{c} are the coefficients of the molecular and convective diffusion of vapor, respectively; ρ_{w} is the water density; and ΔC_v is the difference between the values of the volume masses (densities) of the background vapor and the saturated vapor over the droplet surface.

For a qualitative estimation of D_{c}, we will use its direct correlation with the energy of turbulence. The mean turbulent energy falling on the unit of the cloud volume is controlled by the number of simultaneously freezing droplets contained in it and is

$$\varepsilon(a) = E_0(a)\tau N'_{\mathrm{FT}}. \tag{12}$$

Here, τ is the effective time of turbulence decay in the zone of disturbance around the frozen droplet. By analogy with the determination of the molecular diffusion coefficient, the quantity D_{c} will be represented in the form $D_{\mathrm{c}} \approx \frac{1}{3}ul$, where u is the characteristic velocity of turbulent motions and l is their characteristic scale. The quantity u will be estimated from the equality $u^2 = \frac{\varepsilon(a)}{2\rho_{\mathrm{a}}}$, where ρ_{a} is the air density, whence we obtain

$\varepsilon(a) = \dfrac{18D_c^2\rho_a}{l^2}$. After the substitution of this expression into (12), as well as into (5), (10), and (11) with $D_m = 0$, we obtain the equation whose solution yields

$$D_c = Ba^{2.7}\exp(-0.6T), \tag{13}$$

where

$$B \approx 0.05\frac{N_0\tau\rho_i L_f(T)}{a_0^{1.7}\rho_w\rho_a}l^2\Delta C_v \tag{14}$$

is the dimension factor, which is virtually temperature-independent if $T > -35$°C.

As (13) shows, the second term of the sum in (11), which is due to the effect of freezing of water-1 droplets, increases rapidly with both the enlargement of droplets and the temperature decrease. When the quantity D_c begins to exceed D_m, the regime of particle growth changes to the convective-diffusion regime.

The ascending motion in a cloud that arises from air heating and sustains the condition $\Delta C_v > 0$ is another well-known factor accelerating the particle growth during the freezing of droplets. The release of vapor by freezing droplets favors the fulfillment of this condition.

We considered the growth of water-1 droplets alone, leaving aside ice particles and A-water droplets. Under the conditions when the molecular-diffusion mass exchange prevails in the cloud, the specified particles grow several times faster than water-1 droplets owing to the supersaturation of vapor over these particles. As is already mentioned, only a small fraction of such particles experience a substantially leading growth in local zones of microscale turbulence. The time of their growth to the sizes ensuring irreversibility of the phase-disperse restructuring of the cloud is inversely proportional to the growth rate and, in accordance with (11) and (13), must decrease with decreasing temperature approximately as a decreasing exponent does. The experimental data presented in Fig. 3 demonstrate a similar behavior.

It should be noted that, under the action of reactive recoil in the case of nonsymmetrically outflowing vapor, the freezing droplets acquire a momentum, a result that can lead to the deviation of their shape from the initial sphericity, to their collision and coalescence with other droplets, and to their settling on ice crystals. Evidently, these accompanying effects must be most strongly pronounced in such a cloud that contains large droplets of A-water. Diversity and sometimes fancifulness of shapes of a certain part of ice particles, which are the products of freezing of such droplets, [17] clearly indicate in what way the above dynamic processes proceed in a natural cloud.

Now, a few words will be devoted to the physics of artificial modification of processes in cold clouds by their seeding with an ice-forming reagent. A significant presence of A-water in mixed and even ice (according to traditional notions) clouds [4] readily explains the positive effect of their seeding by the same action of a chemical reagent on both metastable forms of water. In light of the aforementioned, it seems that this effect is physically caused by an increase in the amount of simultaneously freezing droplets that excite the microscale turbulence in a cloud, with all the consequences described above, rather than by a simple increase in the concentration of ice particles that compete with one another in their growth. It is this circumstance that explains a rapid enlargement of ice particles, which ensures a fairly prompt artificial increase of precipitation from the cloud. However, it should be noted that not only the freezing of droplets can be a zone of microscale disturbances. These disturbances can be caused as well by the means of reagent delivery directly into a cloud (pyrotechnic cartridges) as well as by an airplane, which, in the process of action, flies either inside the cloud or slightly above its upper boundary. In any case, the effect of precipitation from a supercooled cloud during a simple passage of an airplane through it has long been noted and discussed in the literature [18].

6. CONCLUSIONS

Such apparent paradoxes as the preservation of the spherical shape of droplets at different densities of the adjacent phases and the expected overheating at the crystallization front above the melting point of ice are associated with the freezing (crystallization) of liquid water droplets in a metastable (supercooled or amorphous) state. An improved model of frontal crystallization was proposed in this study. This model is based on the fact that the solid phase, which is formed behind the crystallization front, retains the volume of the liquid phase rather than its mass by reason of a continuous interphase cohesion through hydrogen bonds. The fraction of water excessive with respect to ice is separated from the crystallization front in the form of free molecules escaping through the liquid into the gaseous medium. The entire released energy of the phase transition is transferred to these molecules as the kinetic energy. As a result, the initial temperature of the liquid remains constant at the crystallization front and behind it and the energy of molecules leaving the liquid is characterized by their velocity of tens of meters per second.

A model of the latent energy of freezing of supercooled water as a function of temperature suggesting the vanishing of this energy at the point of homogeneous freezing of water (about –39°C) is physically substantiated in the course of analysis.

It is important for the physics of clouds that a high-rate vapor outflow from the freezing droplet generates a zone of microscale turbulence around it. This turbulence sharply accelerates the mass exchange between the particles encompassed by it and vapor through the transition to convective diffusion of vapor. Owing to an increase in the probability of freezing of droplets with an increase in their sizes, the process of their freezing in a developing stratiform cloud is continuous in time. In the field of zonal disturbances, a small part of ice crystals and A-water droplets accompanying them experience the leading growth and their accelerating gravitational settling results in irreversible and continuous disturbances. The process is ended in a complete evaporation of ordinary water droplets and the transition of a cloud to a phase-mixed state in which the liquid disperse phase is represented by A-water droplets. The well-known shortening of the initial fine-dispersed stage of the evolution of clouds with their temperature lowering can be explained only by the development of microscale disturbances arising from the freezing of droplets.

All conclusions of this study are based on analysis of natural phenomena with the use of elementary physical concepts. The elaborated version of the crystallization mechanism of metastable liquid water is additionally validated by the results of well-known laboratory experiments on investigation of an amorphous water condensate. Further deepening and development of investigations of metastable states of water and the effects of their crystallization that are based on laboratory experiments seem an expedient and feasible task, which is equally important for both the physics of water and the physics of clouds. We hope that all considerations presented in this paper will be helpful in choosing the direction for experimental quests.

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