Homogeneous Ice Nucleation Rate in Supercooled Droplets of Aqueous Solutions

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Abstract—The homogeneous ice nucleation rate in the pure water and aqueous solutions is investigated. Experimental data of different authors are analyzed. The attempt to draw up a uniform theoretical description of the crystallization process of aqueous solutions on the basis of analyzed data is made.

INTRODUCTION

It is known that water can be in supercooled state, i.e., it can remain liquid at the temperature much lower than the melting temperature, especially if it is not in contact with any solid surface which could favor the crystallization process. The considerable number of supercooled droplets can be present in the stratosphere and in the upper troposphere that is caused by conditions of the water phase transition because the homogeneous crystallization is the controlling mechanism for the formation of high clouds considerably influencing the Earth's climate in the upper troposphere by means of the scattering and absorption of solar and Earth's radiation.

The phase equilibrium of water–ice system is well studied that is confirmed by the numerous data. The detailed theoretical description of this process based on the principles of thermodynamics is available. However, a completely different situation emerges when describing the homogeneous phase transition rate. According to the classic theory, the phase transition is initiated by the solid phase nucleation inside the liquid phase. For the further growth and for the phase transition completion these nuclei should be of the size larger than the critical one, i.e., the energy barrier should be overcome. The number of nuclei of the critical size being formed in the unit of volume per the unit of time is the measure of ice nucleation rate.

During recent 50 years, a great number of experiments on the investigation of homogeneous nucleation rate in supercooled water were carried out. But till now, the process of homogeneous crystallization of cloud droplets is not still completely studied. Many experimental data are coordinated with theoretical computations but considerable errors are present. The difference between the observed and computed data is a big problem. There is no physical model of liquid water taking account of its all exceptional properties.

This work is the attempt of the uniform theoretical description of the great diversity of experimental data on the homogeneous ice nucleation rate in supercooled water. The main objective is the generalization of investigations carried out during several recent decades and the derivation of the correct formula for the description of the homogeneous ice nucleation rate in aqueous solution droplets.

1. THE DEPENDENCE OF ICE MELTING TEMPERATURE ON THE WATER ACTIVITY

In the approach used in this work, the important role belongs to the dependence of ice melting temperature on the presence of solutes. The value of the melting temperature T_0 can be derived from the condition of the equality of the water vapor saturation pressure over the solution surface and the saturation pressure over the ice surface:

$$E_{ws}(T_0)a_w = E_{is}(T_0),$$

where a_w is the water activity being the quantitative measure of solutes in the water. For pure water ($a_w = 1$), the melting temperature is equal to 273.16 K. If the solute content in the water increases ($a_w < 1$), the saturation pressure over the solution surface decreases, hence, the equality of pressure over the solution and
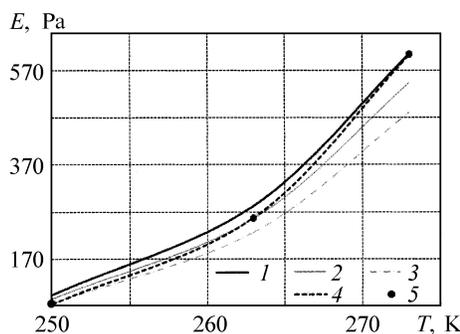
Fig. 1. The influence of solutes on the melting temperature. (*1*) $a_w = 1$; (*2*) $a_w = 0.9$; (*3*) $a_w = 0.8$; (*4*) E_{is}; (*5*) T_0.
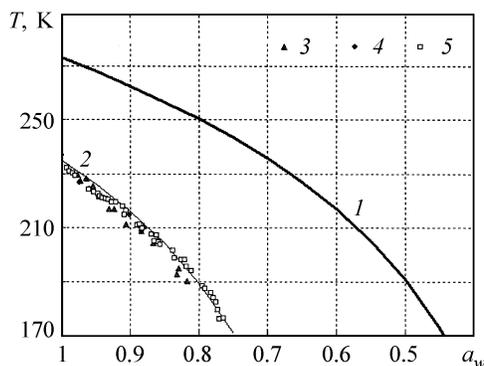

Fig. 2. The dependence of the melting temperature and crystallization temperature on the water activity. (*1*) T_0; (*2*) T_c; (*3*) the data of [25]; (*4*) the data of [16]; (*5*) the data of [13].

over the ice is observed at lower temperature that is demonstrated in Fig. 1. In the figure it is clear that, for example, at $a_w = 1$ the saturation pressure over the ice and the saturation pressure over the solution turn to be equal at $T_0 = 273.16$ K, and at $a_w = 0.8$ they turn to be equal at $T_0 = 250.16$ K.

On the basis of the data of [16], the formula describing the dependence of the ice melting temperature on the water activity is proposed:

$$T_0 = 273.16 + 103.6\ln(a_w) + 15.613\ln^2(a_w) + 54.118\ln^3(a_w). \tag{1}$$

The dependence of the melting temperature on the water activity obtained from formula (1) is given in Fig. 2. It is clear that the presence of solutes in water leads to the considerable decrease in the melting temperature.

2. THE DEPENDENCE OF SOLUTION DROPLET CRYSTALLIZATION TEMPERATURE ON THE WATER ACTIVITY

In this work, the temperature corresponding to the freezing of a half of all solution droplets is meant to be the homogeneous crystallization temperature T_c. As a result of recent investigations of crystallization process [4, 13, 25], the experimental data on the homogeneous solution crystallization temperature were obtained [13]. The investigations of experimental data for some solutions revealed the direct dependence between the homogeneous crystallization temperature decrease and the melting temperature decrease. As a result, on the basis of the data of [13], the formula to compute the homogeneous crystallization temperature being analogous to formula (1) is proposed:

$$T_c^{\text{hom}} = 273.16 + 103.6\ln(a_w - 0.305) + 15.613\ln^2(a_w - 0.305) + 54.118\ln^3(a_w - 0.305). \tag{2}$$

The numerical value of 0.305 is derived in [13]. In Fig. 2, the results of experiments on the homogeneous crystallization temperature determination and the results of approximation of formula (2) are given.

It follows from the figure analysis that the approximating dependence can describe the data of experimental investigations with an accuracy being satisfactory for the practice.

3. THE HOMOGENEOUS ICE NUCLEATION RATE IN PURE WATER

The number of ice crystals being formed in the unit of volume of the pure supercooled water per the unit of time is called the homogeneous nucleation rate in the pure water whose dependence on the temperature is described by the classic formula [2, 14, 16, 20]

$$J_{wi}^{hom} = J_0^{hom} \exp\left[\frac{-\Delta G_{wi}^{max}}{kT}\right]\exp\left[\frac{-\Delta G_{act}}{kT}\right],$$ (3)

where J_{wi}^{hom} is the homogeneous nucleation rate (m^{-3} s^{-1}); J_0^{hom} is the multiplier (m^{-3} s^{-1}); ΔG_{wi}^{max} is the energy spent for the generation of ice crystals of the critical size in the water (J); k is Boltzmann constant (J/K); T is the temperature (K); ΔG_{act} is the activation energy (J).

The multiplier J_0^{hom} in formula (3) is derived from the expression from [14, 16, 20]

$$J_0^{hom} = 2\left(\frac{\rho_w}{m_w}\right)^{2/3}\left(\frac{\rho_w}{\rho_i}\right)\left(\frac{kT}{h}\right)\left(\frac{\sigma_{wi}}{kT}\right)^{1/2},$$ (4)

where m_w is water molecule mass (kg); ρ_w is the water density (kg/m^3); ρ_i is the ice density (kg/m^3); σ_{wi} is the specific surface energy at the water–ice boundary (J/m^2); h is Planck constant (J/s).

The phase transition starts with the solid phase nucleation inside the liquid phase. These nuclei should be of the size larger than the critical one for their further growth and phase transition completion. The radius of the ice crystal of critical size is described by the following expression from [2]:

$$r_{cr} = \frac{2\sigma_{wi}m_w}{r_i L_{wi} \ln(T_0/T)},$$ (5)

where L_{wi} is the latent crystallization heat (6.7×10^{-21} J).

The energy spent to generate the ice crystals of the critical size in the water is derived from the formula from [2]

$$\Delta G_{wi}^{max} = \frac{4}{3}\pi r_{cr}^2 \sigma_{wi}\omega,$$ (6)

where ω is the coefficient depending on the shape of the crystal being formed ($\omega \geq 1$).

The dependence of the specific surface energy and of the ice density on the temperature can be approximated by formulas from [3]:

$$\sigma_{wi} = -0.0397875 + 0.00025T,$$ (7)

$$\rho_i = 956.58 - 0.144886T.$$ (8)

The energy needed to break the hydrogen bond in the liquid is called the activation energy ΔG_{act} and is determined by the following expression [24]:

$$\Delta G_{act} = 3.6 \times 10^{-20} - 7.3 \times 10^{-22}(T - T_0).$$ (9)

4. THE HOMOGENEOUS ICE NUCLEATION RATE IN THE AQUEOUS SOLUTION

Rather recently, Koop et al. [13] developed the thermodynamic model for the homogeneous crystallization of aqueous solution. Authors showed that the homogeneous ice nucleation in aqueous solutions depends on the solution activity only, but not on its nature. Authors [13] also revealed that the solution presence or taking account of pressure have very similar influence on the nucleation rate. It is proposed to compute the homogeneous ice nucleation rate in supercooled solution droplets ($a_w < 1$) using the formula being analogous to the formula of the ice nucleation rate in the pure water:
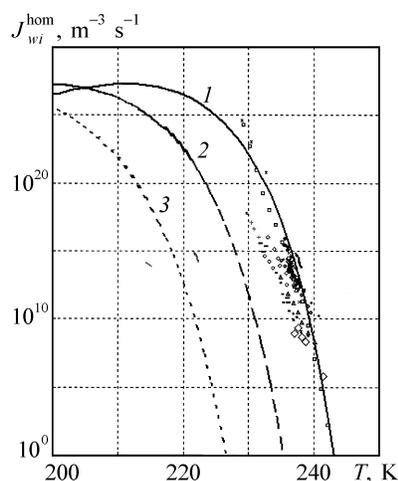
Fig. 3. The dependence of the homogeneous ice nucleation rate on the temperature and activity of water. Computations using formula (10) at a_w equal to (*1*) 1.0, (*2*) 0.95, (*3*) 0.9. The data of [16] (a_w = 0.904; 0.946; 1.0) and of [5–12, 14, 15, 18–23] (a_w = 1.0) are shown with signs.

$$J_{wi}^{hom} = J_0^{hom} \exp\left[\frac{-\Delta G_{wi}^{max}}{kT'}\right] \exp\left[\frac{-\Delta G_{act}}{kT'}\right], \qquad (10)$$

where T' is the air temperature at which the homogeneous nucleation rate in the solution is equal to that in the pure water at temperature T. The introduced parameter T' takes a simultaneous account of the influence of temperature and of aqueous solution activity. To compute it, it is proposed to use the following formula:

$$T' = 273.16 + 103.6\ln(1 - a_w + a_w^*) + 15.613\ln^2(1 - a_w + a_w^*) + 54.118\ln^3(1 - a_w + a_w^*), \qquad (11)$$

where a_w^* is the equilibrium value of water activity derived from the formula from [17]:

$$a_w^* = \exp\left(\frac{210368 + 131.48T - 3323730/T - 41729.1\ln(T)}{8.31441T}\right). \qquad (12)$$

In Fig. 3, the dependence of the homogeneous ice nucleation rate on the temperature and activity of water computed from formula (10) is represented. The data of experiments carried out during several decades are also drawn there. It is clear that the maximum number of experiments was carried out for the pure water and for the initial stage of homogeneous crystallization. The current data [10, 11, 14, 16, 21, 23] have higher values of nucleation rate as compared with the data of earlier experiments [5–9, 11, 12, 15, 18] that can be explained by the insufficient purification of samples for which the water activity was less than unity. It follows from the figure that the proposed theoretical dependence (10) describes accurately enough the current experimental data. In Fig. 3, the experimental data on the nucleation rate in aqueous solutions obtained by Larson and Swanson [16] are also represented. Considerably lower values of nucleation rate in this work as compared with the proposed theoretical dependence (10) are caused by the peculiarities in the experiment carrying out as a result of which the temperature values of homogeneous solution crystallization obtained by authors turned out to be much lower as compared with similar experiments, that indicates the small nucleation rate.

On the whole, it is clear that if the solute content in the water increases, the nucleation rate considerably decreases and the droplet crystallization takes place at lower temperature.

5. THE RESULTS OF NUMERICAL MODELING OF AQUEOUS SOLUTION DROPLET CRYSTALLIZATION PROCESS

When implementing the numerical modeling of the crystallization process of supercooled droplets, the following suppositions are used:

—the environment is assumed to be homogeneous and isotropic;
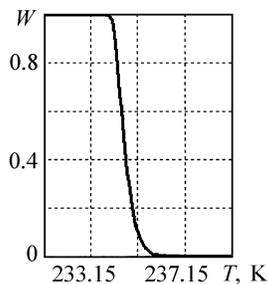
Fig. 4. The dependence of the portion of frozen droplets on the temperature.
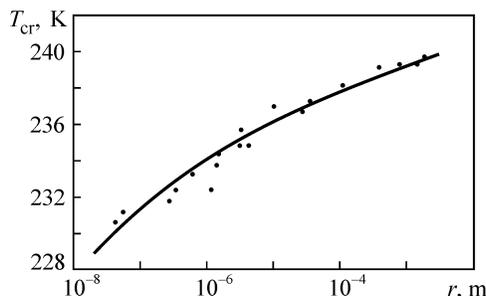
Fig. 5. The dependence of the crystallization temperature on the solution droplet radius.

—the thermal effects associated with water phase transitions do not influence the continuum due to their low intensity;

—the cloud of supercooled droplets is monodisperse;

—the processes of diffusion growth and coagulation of particles are absent;

—the droplet crystallization is the only source of crystal generation.

The above suppositions enable to write down the equation for the droplet crystallization rate according to [1] in the following way

$$\frac{dW}{dT} = \frac{(4/3)\pi r^3 J_{wi}^{hom}(1-W)}{dT/d\tau},$$
(13)

where r is the droplet radius (m); W is the portion of the frozen droplets; $dT/d\tau$ is the air cooling rate (K/s).

The crystallization process modeling was carried out by the numerical integration of formula (13) taking account of the proposed formula (10) by means of the method of rectangles at the initial temperature $T = 273.15$ K assuming that only the droplets exist in the beginning of the process, i.e., $W = 0$.

The computation results of the dependence $W(T)$ at $r = 1$ μm and $dT/d\tau = -1$ K/s are represented in Fig. 4 from which it is clear that the droplet crystallization occurs within the narrow range of temperature values. The position of this range depends on the size of crystallized droplets, on their cooling rate and water activity. The computation results of crystallization temperature at which the portion of frozen droplets reaches the value $W = 0.5$ for the solution droplets of the radius of 2.5 μm at $dT/d\tau = -1$ K/s depending on the water activity are represented in Fig. 2 in the form of the solid fine curve well describing the experimental data and practically coincides with the empirical dependence (2). In Fig. 5, the results are given of the crystallization temperature determination for the pure water droplets within the droplet radius range from 20 nm to 3 mm at $dT/d\tau = -1$ K/s. The experimental data on the pure water crystallization [20] are represented in the same figure. One can conclude that the proposed formula (10) describes accurately enough the experimental data and can be used at the numerical modeling of crystallization processes.

CONCLUSION

In this work, the process of homogeneous water–ice phase transition is considered and the theoretical formula to compute the homogeneous ice nucleation rate in supercooled solution droplets is proposed describing accurately enough the great number of considered experimental data.

The results of homogeneous crystallization temperature computations describe the experimental data with the accuracy sufficient for the practice that enables to recommend the use of the proposed formula at the numerical modeling of microphysical processes in clouds.

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