MODEL OF CRYSTALLIZATION OF SUPERCOOLED DROPLETS OF AQUEOUS SOLUTIONS

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1. INTRODUCTION

Crystallization of supercooled droplets of water and aqueous solutions play an important role in the formation of upper air clouds, which have a significant influence on Earth's climate by scattering and absorption of solar and terrestrial radiation.
The phase state of upper layer clouds is mostly determined by the homogeneous mechanism of ice nuclei formation. In the lower and middle troposphere, ice crystals appear mainly due to the heterogeneous mechanism of ice nuclei formation on the surface of foreign particles in a volume of supercooled droplets. Recent experimental data suggest that heterogeneous crystallization can play a significant role in the formation of crystals in the upper troposphere.
Model of homogeneous and heterogeneous crystallization of supercooled droplets of aqueous solutions is described in the report.

2. ICE NUCLEATON RATE

In our model we suggest to estimate rate of homogeneous and heterogeneous ice nuclei formation in supercooled droplets of solutions using the classical expression for calculation of ice nuclei rate formation in pure water but taking into account presence of soluble.
The basis of the proposed model is the assumption of the constancy of the ice nucleation rate while temperature changes by law like dependence of ice melting temperature T_0 on water activity a_w:

$$T_0 = 273.16 + 103.6\ln(a_w) + 15.6\ln^2(a_w) + 54.1\ln^3(a_w) .$$

We have introduced an empirical parameter with dimension of temperature, taking into account the effect of solutes and temperature on formation of ice nuclei in the droplets of aqueous solutions:

$$T' = 273.16 + 103.6\ln(1 - a_w + a_w^*) + 15.6\ln^2(1 - a_w + a_w^*) + 54.1\ln^3(1 - a_w + a_w^*) ,$$

where

$$a_w^* = \exp\left[15.8 + \frac{25301.6 - 5018.9\ln(T)}{T} - \frac{399755.4}{T^2}\right]$$

This parameter depends on temperature and water activity as schematically shown in Figure 1.

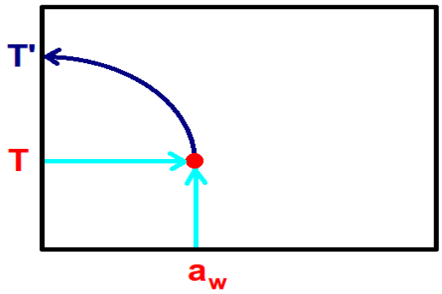

Fig. 1. Parameter T' dependence on temperature and water activity

So, this way makes possible to use classical expression for homogeneous ice nucleation rate

$$J_{wi}^{gom} = J_0^{gom} \exp\left(\frac{-\Delta G_{max}^{gom} - \Delta G_{act}}{k T'}\right) ,$$

$$\Delta G_{max}^{gom} = \frac{16\pi m_w^2 \sigma_{wi}^3}{3\rho_i^2 L_{wi}^2 \ln^2\left(\frac{T_0}{T'}\right)}$$

and for heterogeneous ice nucleation rate

$$J_{wi}^{get} = J_0^{get} \exp\left(\frac{-\Delta G_{max}^{get} - \Delta G_{act}}{k T'}\right) ,$$

$$\Delta G_{max}^{get} = \frac{\pi \alpha^2 m_w^{2/3}}{\rho_w^{2/3} L_{wi} \ln\left(\frac{T_0}{T'}\right)} .$$

To characterize the properties of the substrates in the droplets of supercooled aqueous solutions we use the so-called specific linear energy α. Calculated values of α are presented in Table 1.
These data show that substrates like AgI have the lowest values of the specific linear energy.

Table 1. Specific linear energy

Substrate	α (J/m)
$C_{16}H_{33}OH$	$5.75 \cdot 10^{-12}$
AgI	$5.98 \cdot 10^{-12}$
$C_{25}H_{51}OH$	$7.39 \cdot 10^{-12}$
$C_{30}H_{61}OH$	$7.53 \cdot 10^{-12}$
$C_{25}H_{51}OH$	$7.73 \cdot 10^{-12}$
Nanodekanol	$7.84 \cdot 10^{-12}$
$C_{30}H_{61}OH$	$7.91 \cdot 10^{-12}$
$C_{17}H_{35}OH$	$8.96 \cdot 10^{-12}$
Montmorillonite	$1.03 \cdot 10^{-11}$
SiO_2	$1.04 \cdot 10^{-11}$
Kaolinite	$1.06 \cdot 10^{-11}$
OAD	$1.20 \cdot 10^{-11}$

3. CRYSTALLIZATION TEMPERATURE

Numerical simulation of crystallization temperature dependence on the water activity of an aqueous solution carried out and compared with experimental data (Bertram, 2000; Larson, 2006; Koop, 2000; Zuberi, 2002; Zobrist, 2006; Cantrell, 2006). The simulation data confirms that the increase in the concentration of dissolved substances in water leads to a significant decrease in the rate of formation of nuclei and, consequently, the crystallization of drops of the solution occurs at lower temperatures (see Fig. 2 and Fig. 3).

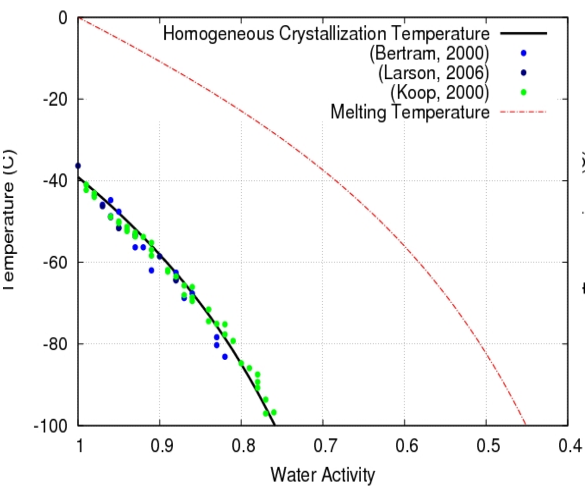

Fig 2. Homogeneous Crystallization Temperature of Droplets of Aqueous Solutions

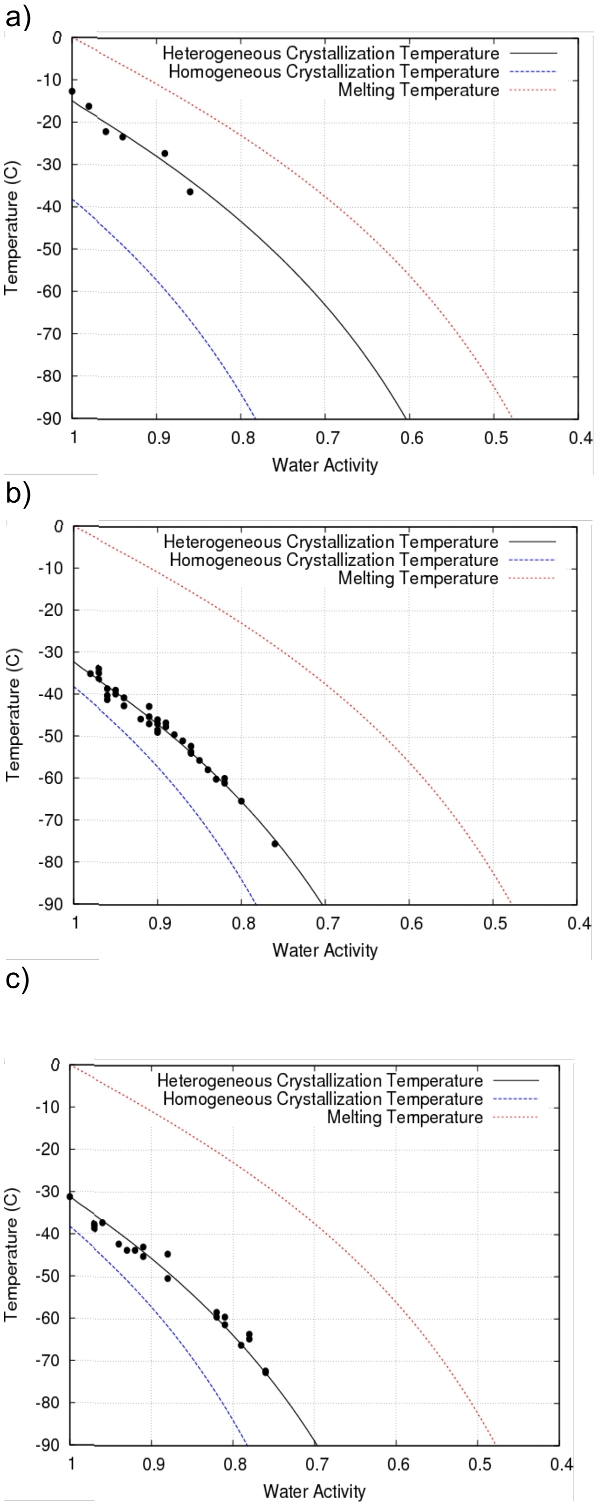

Fig. 3. Heterogeneous Crystallization Temperature of Droplets of Aqueous Solutions: NaCl / C17H35OH (a), (NH4)2SO4 / Kaolinite (b), (NH4)2SO4 / Montmorillonite (c)

Dependence of the heterogeneous crystallization temperature on specific linear energy shows that nucleus of crystallization on the surface of the substrates are flat (see

Fig. 4).

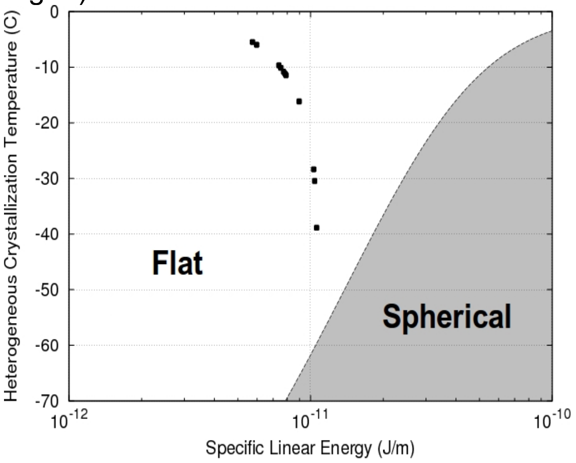

Fig. 4. Heterogeneous Crystallization Temperature as a function of Specific Linear Energy

The accuracy of the crystallization temperature calculation was estimated for the crystallization model (CM), activity model (AM), labmda model (LM). Results of calculation of root mean square errors are presented in Table 2.

Table 2. RMS Errors of Crystallization Temperature Calculation

Solution / Substrate	AM	LM	CM
NaCl / $C_{17}H_{35}OH$	0.8	0.9	0.8
NaCl / $C_{25}H_{51}OH$	1.6	1.0	1.2
NaCl / $C_{30}H_{61}OH$	1.7	1.1	1.2
$(NH_4)_2SO_4$ / $C_{16}H_{33}OH$	1.4	1.5	1.4
$(NH_4)_2SO_4$ / $C_{25}H_{51}OH$	1.9	1.5	0.9
$(NH_4)_2SO_4$ / $C_{30}H_{61}OH$	2.7	1.4	1.7
$(NH_4)_2SO_4$ / Kaolinite	0.5	0.5	0.2
$(NH_4)_2SO_4$ / Montmorillonite	0.9	1.2	0.5
$(NH_4)_2SO_4$ || NaCl || H_2SO_4 / OAD	0.4	0.6	0.3
$NaCH_3CO$ || LiCl || K_2CO_3 / AgI	0.9	1.0	0.7
$(NH_4)_2SO_4$ || NaCl / Nanodekanol	0.5	0.5	0.5
$(NH_4)_2SO_4$ || H_2SO_4 / SiO_2	0.5	0.6	0.5

Accuracy of suggested model is comparable to empiric models one, but our model is more universal because additionally considers dependence on such parameters as cooling rate and surface properties of substrates which in real atmosphere changes significantly and cannot be regarded as constant.

4. CONCLUSION

Calculation results of homogeneous and heterogeneous crystallization temperatures describes experimental data with enough accuracy for practical purposes. This fact allows to recommend the usage of suggested formulas for numerical modeling of microphysical processes in clouds.

5. BIBLIOGRAPHY

Bertram, A.K., T. Koop, L.T. Molina and M.J. Molina, 2000: Ice formation in $(NH_4)_2SO_4$-H_2O particles, J. Phys. Chem. A., 104, 584–588.

Cantrell, W. and C. Robinson, 2006: Heterogeneous freezing of ammonium sulfate and sodium chloride solutions by long chain alcohols, Geoph. Res. Lett., 33, L07802.

Koop, T., B. Luo, A. Tsias and T. Peter, 2000: Water activity as the determinant for homogeneous ice nucleation in aqueous solution, Nature, 406, 611–614.

Larson, B.H. and B.D. Swanson, 2006: Experimental Investigation of the Homogeneous Freezing of Aqueous Ammonium Sulfate Droplets, J. Phys. Chem. A., 110, 1907–1916.

Zobrist, B., 2006: Heterogeneous ice nucleation in upper tropospheric aerosols, Dissetration for the degree of Doctor of Natural Sciences, Zurich, 135.

Zuberi, B., A.K. Bertram, C.A. Cassa, L.T. Molina and M.J. Molina, 2002: Heterogeneous nucleation of ice in $(NH_4)_2SO_4$–H_2O particles with mineral dust immersions, Geophys. Res. Lett., 29, 142-1–142-4.

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