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## FREEZING OF WATER DROPLETS SEEDED WITH ATMOSPHERIC AEROSOLS AND ICE NUCLEATION ACTIVITY OF THE AEROSOLS

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**Abstract**—A method is proposed for analysing the kinetics of droplet freezing, which makes it possible to determine the nucleation rate from the temperature derivative of the logarithm of the relative number of unfrozen droplets. Experiments were carried out by freezing droplets of distilled water either unseeded or seeded with aerosol dust, and by employing this method the ice nucleation rate was determined. It was found that while in the unseeded droplets ice nucleation is controlled by only one type of nucleation-active centre, in the seeded droplets it is stimulated by the presence of three new types of active centres introduced by the aerosol seeds. Each type of active centre is characterized quantitatively by an activity factor and a corresponding “wetting” angle. The theoretically expected linear dependence of the nucleation rate on the concentration of aerosol seeds is experimentally confirmed and the relative number of the aerosol-introduced active centres is calculated.

### 1. INTRODUCTION

The atmospheric pollution by aerosol particles resulting from human activity (e.g. transport, industry, etc.) is usually studied by collecting rainfall or snowfall precipitates and smoke or dust aerosols. For laboratory determination of their ice nucleation activity expansion, diffusion and mixing cloud chambers, different drop freezing techniques, etc. are used (see Boucher, 1969; Valy, 1985, and references therein). The results of the characterization of the atmospheric particles obtained by various authors show discrepancies which are often due to the complex and unclarified physical processes taking place in the natural systems.

There exist many theoretical and experimental studies on the process of droplet freezing (Bigg, 1953a, b; Mason, 1957; Walton, 1969; Boucher, 1969; Clausse, 1985; Kashchiev *et al.*, 1994). The so-called bulk (or immersion) freezing in which the nucleating agent is suspended in the bulk of the droplet is investigated by different experimental techniques, e.g. by the emulsion method (Bigg, 1953a, b; Clausse, 1985; Clausse *et al.*, 1987, 1990), by injection of particles in a fog chamber (Bashkirova and Pershina, 1965), by freezing of suspended droplets (Genadiev, 1970; Spengler and Gokhale, 1972) or of droplets resting on a substrate (Mason, 1957; Dubrovski and Skoloud, 1989), etc. The last method, employed in this work, has the advantage to give more reliable statistical data, since freezing events are averaged over an ensemble of droplets.

In the present investigation an attempt is made to use the classical nucleation theory for describing the kinetics of freezing of water droplets unseeded or seeded with atmospheric aerosols. The aim is to propose a method for experimental determination of the nucleation rate in freezing droplets, to employ the method for obtaining the ice nucleation rate, to characterize quantitatively the nucleation activity of the aerosols and to verify the theoretically expected linear dependence of the nucleation rate on the aerosol concentration.

## 2. FORMULATION OF THE PROBLEM

Let us consider the crystallization of an ensemble of  $N_0$  identical equally sized droplets of volume  $v$  undercooled at a constant rate  $q$ . According to the nucleation theory (Volmer, 1939; Walton, 1969; Toshev, 1973), below the melting temperature  $T_m$  nuclei of the stable solid phase appear by fluctuations within the metastable liquid phase. Nucleation is homogeneous if the nuclei are formed in the bulk of the liquid without the help of foreign molecules or particles, and is heterogeneous if the nuclei are formed in contact with foreign molecules or at the interface between the liquid and available foreign particles or substrates. The theory allows the nucleation rate to be determined in the cases of both homogeneous and heterogeneous nucleation.

The number of nuclei formed in the investigated system is exactly equal to the number  $N$  of frozen droplets in the case of crystallization by the mononuclear mechanism, when each droplet freezes immediately after the appearance of the first nucleus. In Appendix A it is shown that the present experiments satisfy the known criterion (Kashchiev *et al.*, 1991) for the operativeness of this mechanism. If the nucleation events in the separate droplets are independent, i.e. if the freezing of any of the droplets is not influenced by the freezing of the others, the number  $dN$  of frozen droplets during time  $dt$  will be given by (e.g. Clause, 1985; Clause *et al.*, 1990)

$$dN(t) = [N_0 - N(t)]vJ(t)dt, \quad (1)$$

where  $J(\text{m}^{-3}\text{s}^{-1})$  is the nucleation rate.

At constant cooling rate  $q > 0$  the absolute droplet temperature  $T$  decreases with time  $t$  according to  $T(t) = T_m - qt$ , so that  $dT = -qdt$  and  $J = J(T)$ . Equation (1) then becomes

$$dN(T) = -(v/q)[N_0 - N(T)]J(T)dT \quad (2)$$

and integration from  $T_m$  to  $T$  under condition  $N(T_m) = 0$  gives (Bigg, 1953a, b; Clause, 1985; Clause *et al.*, 1987, 1990)

$$N(T) = N_0 \left\{ 1 - \exp \left[ - (v/q) \int_T^{T_m} J(T')dT' \right] \right\}, \quad (3)$$

where  $N(T)$  is the number of all droplets frozen until time  $t$ , i.e. during undercooling from  $T_m$  to  $T \leq T_m$ . Rearranging equation (3), taking the logarithm and differentiating leads to

$$J(T) = (q/v) \frac{d}{dT} \ln [1 - N(T)/N_0]. \quad (4)$$

Equation (4) shows that the experimental determination of the temperature dependence of the nucleation rate  $J$  at known droplet volume  $v$  and constant cooling rate  $q$  reduces to finding the temperature derivative of the experimentally obtainable quantity  $\ln(1 - N/N_0)$ . It should be emphasized that equation (4) is applicable to any kind of time-dependent nucleation, because its derivation does not rely on concrete assumptions about the character of the time dependence of  $J$ . In particular, equation (4) can be very useful for determination of the rate of non-steady-state nucleation (Kashchiev, 1969, 1970, 1984) which may occur in more viscous liquids.

## 3. THEORETICAL RESULTS FOR THE NUCLEATION RATE

The steady-state rate of isothermal nucleation can generally be presented as (Volmer, 1939; Walton, 1969; Boucher, 1969)

$$J(T) = A(T) \exp[-W^*(T)/kT], \quad (5)$$

where  $k$  is the Boltzmann constant,  $W^*$  is the nucleation work and  $A(\text{m}^{-3}\text{s}^{-1})$  is a kinetic factor whose temperature dependence is usually weaker than that of the exponential term.

In non-isothermal nucleation the temperature  $T$  depends on time  $t$  and the nucleation rate  $J$  can be a complex function of  $t$  both through the temperature and directly due to

non-steady state effects (Kashchiev, 1970, 1984; Kozisek and Chvoj, 1989; Kozisek, 1990). In this case  $J$  obtains its simplest form in the scope of the quasi-steady state approximation (Kashchiev, 1970, 1984) which states that it depends on  $t$  only indirectly through  $T$ , i.e.  $J(t) = J[T(t)]$ . This approximation is valid only at a sufficiently small cooling rate  $q$  and allows equation (5) to be used in equations (1)–(4).

According to the classical nucleation theory (Walton, 1969; Toschev, 1973; Kashchiev, 1984; Gutzow *et al.*, 1985)

$$A(T) = z f N_a. \quad (6)$$

Here  $z \approx 0.01-1$  is the so-called Zeldovich factor given by

$$z = (W^*/3\pi k T n^*)^{1/2}, \quad (7)$$

where  $n^*$  is the number of molecules in the nucleus,  $f$  ( $s^{-1}$ ) is the frequency of attachment of molecules to the nucleus and  $N_a$  ( $m^{-3}$ ) is the concentration of active centres on which nuclei can be formed. If the number of attachment sites of molecules on the nucleus surface is  $n_s^*$  and the impingement rate of molecules per site of the nucleus surface is  $kT/\eta v_m$ ,  $f$  can be presented as (Gutzow *et al.*, 1985)

$$f = n_s^* \beta k T / \eta v_m \quad (8)$$

where  $\eta$  is the viscosity of the liquid,  $v_m$  is the molecular volume, and the numerical factor  $\beta \leq 1$  accounts for the local change in the viscosity of the liquid around the nucleus and/or for the hindrances accompanying the incorporation of molecules into the nucleus. Thus, combining equations (6) and (8) gives

$$A = z n_s^* \beta (k T / \eta v_m) N_a. \quad (9)$$

The classical nucleation theory (e.g. Walton, 1969; Toschev, 1973) yields  $W^*$  and  $n^*$  in the form

$$W^* = \alpha \sigma_{ef}^3 v_m^2 / \Delta \mu^2, \quad (10)$$

$$n^* = 2 W^* / \Delta \mu. \quad (11)$$

Here  $\Delta \mu$  is the difference between the chemical potentials of the molecules in the liquid and in the crystal,  $\alpha$  is a numerical shape factor (e.g.  $\alpha = 16\pi/3$  for spherical nuclei;  $\alpha = 32$  for cubic nuclei, etc.), and  $\sigma_{ef}$  ( $J m^{-2}$ ) is an effective specific surface free energy. In the case of homogeneous nucleation  $\sigma_{ef} = \sigma$ ,  $\sigma$  being the specific surface free energy of the liquid/nucleus interface. In the case of heterogeneous nucleation  $\sigma_{ef} < \sigma$  and if the relation between  $\sigma_{ef}$  and  $\sigma$  is presented as

$$\sigma_{ef}^3 = \Phi \sigma^3, \quad (12)$$

the factor  $\Phi$  ( $0 \leq \Phi \leq 1$ ) can be used as a parameter for quantitative characterization of the nucleation activity of the active centres. Different theoretical models give different expressions for  $\Phi$ . For instance, if a spherical cap-shaped nucleus is formed on a flat surface,  $\Phi$  is the following function of the angle  $\theta$  of “wetting” of the surface by the nucleus (Volmer, 1939):

$$\Phi(\theta) = (1/4)(2 + \cos \theta)(1 - \cos \theta)^2. \quad (13)$$

In this case,  $\Phi = 1$  at non-wetting ( $\theta = 180^\circ$ ), i.e. in homogeneous nucleation, and  $\Phi = 0.5$  at half-wetting ( $\theta = 90^\circ$ ) and  $\Phi = 0$  at full wetting ( $\theta = 0$ ), which are two concrete examples of heterogeneous nucleation.

In the case of melt crystallization  $\Delta \mu$  depends on the melting entropy  $\Delta S_m$  and the supercooling  $\Delta T = T_m - T$  in the system. In the Kelvin approximation  $\Delta \mu = \Delta S_m \Delta T$ . As shown by Toner and Gravalho (1990), for freezing of water the Hoffman approximation is a better one:

$$\Delta \mu = \Delta S_m T \Delta T / T_m. \quad (14)$$

Combining equations (5), (9), (10) and (14) results in the following expression for the steady-state nucleation rate to be used hereafter:

$$J(T) = z n_s^* \beta (k T / \eta v_m) N_a \exp(-\alpha \sigma_{ef}^3 v_m^2 T_m^2 / \Delta S_m^2 k T^3 \Delta T^2). \quad (15)$$

#### 4. EXPERIMENTAL TECHNIQUE

The present investigation was carried out with a dust-like aerosol collected with the help of a brush from the smooth surface of a lee protected against rainfall and situated 1.5 m above the ground of a busy traffic crossing in Sofia (Bulgaria). Examination of the aerosol dust by optical microscope showed polyhedrally shaped particles with diameters less than about 10  $\mu\text{m}$  and a diameter distribution with a maximum at about 1.5  $\mu\text{m}$ . Microprobe analysis of the aerosol dust gave evidence for the presence of about 52 wt % Si, 20 wt % Fe, 11 wt % Al, 9 wt % Ca, 3 wt % K and 0.1 to 1 wt % Cu, Zn, Ti and Mn. Other physicochemical characteristics of the dust are not available.

The freezing of droplets of distilled water and of such droplets seeded with the aerosol dust of three different concentrations was investigated. Before each experiment with seeded droplets the freshly prepared water–dust suspension was homogenized by long shaking. The temperature dependence of the number of water droplets frozen as a result of undercooling of the droplet ensemble at a constant rate was determined experimentally. The apparatus and the experimental technique used are briefly described by their authors (Dubrovski and Skoloud, 1988, 1989; Bilkova *et al.*, 1989). In each experiment, about 100 water droplets were placed on thin polyethylene foil adhering to a thick cooling metal plate. The average droplet volume was  $v = (0.95 \pm 0.07) \text{ mm}^3$  and the distance between the droplets prevented them from interacting. The droplets were observed through a heat insulating window by a TV camera which could distinguish if they were frozen or not. The camera was connected to a computer which controlled the cooling rate and, after every 2 s, recorded the number of frozen droplets. The temperature decreased linearly from the melting point  $T_m = 273.15 \text{ K}$  to  $T = 248 \text{ K}$  at a rate  $q$  from 0.05 to 0.07  $\text{K s}^{-1}$ . According to Dubrovski and Skoloud (1989), the accuracy in measuring the temperature is  $\pm 0.15 \text{ K}$ . For calculating  $J$  from the experimental data, the average value for  $q/v = 65 \text{ K s}^{-1} \text{ cm}^{-3}$  was used.

#### 5. EXPERIMENTAL DATA FOR UNSEEDED WATER DROPLETS

##### 5.1. Method of analysing

If the investigated unseeded droplets of distilled water crystallize by heterogeneous nucleation occurring, e.g. when microscopic foreign particles are present uncontrollably in the water, according to equation (15), the nucleation rate  $J_o$  will be

$$J_o(T) = A_o \exp(-B_o/T^3 \Delta T^2), \quad (16)$$

where

$$A_o = z_o n_{s,o}^* \beta(kT/\eta v_m) N_{a,o}, \quad (17)$$

$$B_o = \alpha v_m^2 \sigma_o^3 T_m^2 / k \Delta S_m^2. \quad (18)$$

Here the subscript “o” indicates that the respective quantity is related to the case of unseeded droplets. For instance,  $\sigma_o$  is the respective effective specific surface energy connected with  $\sigma$  by the relation  $\sigma_o^3 = \Phi_o \sigma^3$ , where  $\Phi_o$  is the respective activity factor. From each  $\Phi_o$ , a characteristic “wetting” angle  $\theta_o$  can be calculated with the help of equation (13). Also,  $N_{a,o} (\text{m}^{-3})$  is the concentration of active centres present initially in the unseeded droplets.

It is seen from equation (16) that when  $\sigma_o$  is practically temperature independent, plotting  $\ln J_o$  vs  $1/T^3 \Delta T^2$  results in the following straight line

$$\ln J_o = \ln A_o - B_o(1/T^3 \Delta T^2). \quad (19)$$

From the slope  $B_o$  and the intercept  $\ln A_o$  both determined by fitting to experimental  $J_o(T)$  data, with the help of equations (17) and (18) one can obtain, respectively,  $\sigma_o$  and  $\beta N_{a,o}$  provided the other parameters are known or evaluated. Using the so-obtained  $\sigma_o$ , the respective activity factor  $\Phi_o$  and “wetting” angle  $\theta_o$  can be calculated.

## 5.2. Analysis of the experimental data

Under the same conditions, a series of nine experiments was carried out on freezing of a population of 98–100 unseeded droplets of distilled water. At intervals of 0.2 K the relative number  $N/N_0$  of frozen droplets was determined in the series which had a total of  $N_0 = 894$  droplets. The most probable temperature of freezing (251.6 K) corresponding to the inflection point of the experimentally obtained  $N(T)$  dependence, was found to be close to that estimated by Bigg (1953a, b) and consistent with the heterogeneous nucleation hypothesis. The respective homogeneous nucleation temperature is lower than 235 K, according to Rasmussen and MacKenzie (1971) and Butorin and Skripov (1972). In Fig. 1, the circles represent the experimentally obtained dependence of  $\ln(1 - N/N_0)$  on  $T$  in the case of unseeded water droplets.

In order to determine the temperature derivative of  $\ln(1 - N/N_0)$  a method for smooth approximation of experimental data was applied. This method, described in detail by Talmi and Gilat (1977), Kупенова (1980) and Kупенова and Stoyanova (1992), is briefly presented in Appendix B. The curve in Fig. 1, passing through the circles, depicts the smooth approximation function for the experiments with unseeded droplets. The nucleation rate  $J_0$  is calculated from equation (4) with the use of the  $q/v$  value in Section 4.

The so-obtained dependence of  $\ln J_0$  on  $1/T^3 \Delta T^2$  is shown in Fig. 2 by circles. In accordance with equation (19), this dependence is linear. The best-fit parameters  $A_0$  and  $B_0$  are given in Table 1. The corresponding straight line in Fig. 2 represents equation (19) with  $A_0$  and  $B_0$  from Table 1.

Using  $B_0$ , the following parameters characterizing the kinetics of heterogeneous ice nucleation in unseeded droplets of distilled water and the active centres present in them were determined: the effective surface free energy  $\sigma_0$  [from equation (18)], the activity factor  $\Phi_0$  [from equation (12)] and the “wetting” angle  $\theta_0$  [from equation (13)]. The values of these parameters are collected in Table 2. Also, the calculated chemical potential difference  $\Delta\mu$  [from equation (14)], nucleation work  $W_0^*$  [from equation (10)] and number  $n_0^*$  of molecules in the ice nucleus [from equation (11)] at the ends of the investigated temperature interval are given in Table 3. All calculations were done with assumed  $\alpha = 16\pi/3$  and the known values of  $\sigma = 20 \text{ mJ m}^{-2}$ ,  $\Delta S_m/k = 2.65$  and  $v_m = 3 \times 10^{-23} \text{ cm}^{-3}$  (Boucher, 1969; Huige and Thijssen, 1969). Using  $A_0$  from Table 1 and the evaluated  $z_0 = 0.01$  [from equation (7)] and  $n_{s,0}^* = 20$  (according to the approximation  $n_{s,0}^* = (n_0^*)^{2/3}$ ) it was possible to calculate also  $\beta N_{a,0}$ . In the case of water Toner and Gravalho (1990) show that  $\eta(T) = 0.139(T/225 - 1)^{-1.64}$  (P). The variation of the viscosity in the investigated temperature interval (from 248 to 267 K) is not large (from 0.006 to 0.002 P), so that  $\eta = 0.005$  P was used in the calculations. Thus, it was found that  $\beta N_{a,0} = (8.4 \pm 1.2) \times 10^{-4} \text{ cm}^{-3}$ .

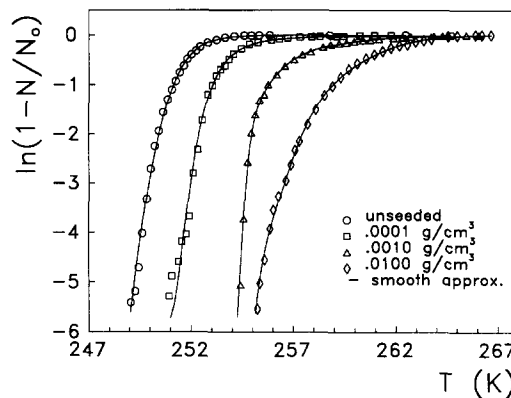


Fig. 1. Temperature dependence of the relative number of unfrozen water droplets unseeded or seeded with atmospheric aerosol (seed concentration indicated): symbols—experimental data, curves—smooth approximation.

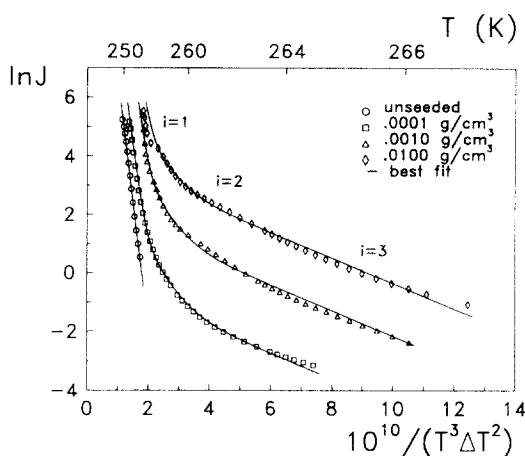


Fig. 2. Dependence of the ice nucleation rate  $J(\text{cm}^{-3} \text{s}^{-1})$  on  $1/T^3 \Delta T^2$  for water droplets unseeded or seeded with atmospheric aerosol (seed concentration indicated): symbols—experimental data, curves—equations (16) and (25).

Table 1. Best-fit parameters  $A_i$  ( $\text{cm}^{-3} \text{s}^{-1}$ ) and  $B_i$  ( $\text{K}^5$ ) for ice nucleation on active centres of type  $i=0, 1, 2, 3$  in water droplets

Droplets	$i$	$\ln A_i$	$B_i \times 10^{10}$
Unseeded	0.	$15.2 \pm 0.1$	$8.5 \pm 0.1$
Seeded	1	$16.1 \pm 2.6$	$8.0 \pm 2.2$
$C = 0.1 \text{ mg cm}^{-3}$	2	$4.7 \pm 2.0$	$2.0 \pm 1.0$
	3	$-0.2 \pm 0.5$	$0.4 \pm 0.1$
Seeded	1	$19.1 \pm 2.7$	$8.0 \pm 2.2$
$C = 1 \text{ mg cm}^{-3}$	2	$6.9 \pm 2.0$	$2.0 \pm 1.0$
	3	$2.2 \pm 0.4$	$0.4 \pm 0.1$
Seeded	1	$20.7 \pm 5.8$	$8.0 \pm 2.2$
$C = 10 \text{ mg cm}^{-3}$	2	$8.4 \pm 2.0$	$2.0 \pm 1.0$
	3	$4.0 \pm 0.4$	$0.4 \pm 0.1$

Table 2. Effective specific surface energy  $\sigma_i$  ( $\text{mJ m}^{-2}$ ), activity factor  $\Phi_i$  and "wetting" angle  $\theta_i^\circ$  for ice nucleation on active centres of type  $i=0, 1, 2, 3$  in water droplets

Droplets	$i$	$\sigma_i$	$\Phi_i$	$\theta_i$
Unseeded	0	$11.2 \pm 0.1$	$0.174 \pm 0.002$	$56.3 \pm 0.2$
Seeded	1	$10.9 \pm 1.0$	$0.164 \pm 0.046$	$55.4 \pm 3.9$
	2	$6.9 \pm 1.2$	$0.042 \pm 0.021$	$39.4 \pm 5.1$
	3	$4.1 \pm 0.2$	$0.009 \pm 0.001$	$26.8 \pm 1.0$

Table 3. Chemical potential difference  $\Delta\mu$ , nucleation work  $W_i^*$  and nucleus size  $n_i^*$  for ice nucleation on active centres of type  $i=0, 1, 2, 3$  in water droplets at the ends of the temperature range in which the centres play a significant role

Droplets	$i$	$T(\text{K})$	$\Delta\mu/kT$	$W_i^*/kT$	$n_i^*$
Unseeded	0	249–255	0.23–0.18	9.4–15.5	80–180
Seeded	1	251–258	0.22–0.15	10.3–20.2	96–270
$C = 0.1 \text{ mg cm}^{-3}$	2	251–263	0.22–0.10	2.6–10.8	24–220
	3	253–265	0.20–0.08	0.66–3.5	7–90
Seeded	1	254–259	0.19–0.14	13.3–22.9	140–330
$C = 1 \text{ mg cm}^{-3}$	2	254–263	0.19–0.10	3.4–10.8	36–220
	3	255–266	0.18–0.07	0.79–4.5	9–130
Seeded	1	255–259	0.18–0.14	14.6–22.9	170–330
$C = 10 \text{ mg cm}^{-3}$	2	255–263	0.18–0.10	3.7–10.8	42–220
	3	255–267	0.18–0.06	0.79–6.0	9–200

An upper limit for  $\beta$  can be evaluated from this finding for  $\beta N_{a,o}$ . In view of the fact that the freezing of each droplet with volume  $v \approx 10^{-3} \text{ cm}^3$  needs the presence of at least one active centre in it, the condition  $v N_{a,o} \geq 1$  is mandatory, i.e.  $N_{a,o} \geq 10^3 \text{ cm}^{-3}$ . As a result, it can be concluded that the change in the viscosity of water around the ice nucleus and/or the hindrances in the incorporation of water molecules into the ice nucleus are characterized by  $\beta \leq 10^{-6}$ .

It may be noted that Gutzow *et al.* (1985) have found a  $\beta$  value of  $10^{-6}$  in the case of crystal nucleation in the glass-forming  $\text{NaPO}_3$  melt. However, it must be fully appreciated that the rather small value of  $\beta$  estimated here may actually reflect the commonly observed failure of the classical nucleation theory to give absolute magnitudes correctly.

## 6. EXPERIMENTAL DATA FOR SEEDED WATER DROPLETS

### 6.1. Method of analysing

The nucleation of ice in the presence of atmospheric aerosol particles in the water droplets can be assumed to be additionally stimulated by new active centres existing on the surface of these particles. Recently, a polymer additive introduced into the solution has been found to play a similar role of offering new nucleation-active centres in  $\text{BaSO}_4$  precipitation (van der Leeden *et al.*, 1993). If there are centres with different ice-nucleation activity, the overall nucleation rate  $J$  will be the sum of  $J_o$  and the nucleation rates  $J_i$  corresponding to the different activities  $i = 1, 2, 3, \dots$ :

$$J = J_o + \sum_i J_i. \quad (20)$$

According to equation (15), the nucleation rate on the centres of  $i$ -type activity is of the form

$$J_i(T) = A_i \exp[-B_i/T^3 \Delta T^2], \quad (21)$$

where

$$A_i = z_i n_{s,i}^* \beta (kT/\eta v_m) N_{a,i}, \quad (22)$$

$$B_i = \alpha v_m^2 \sigma_i^3 T_m^2 / k \Delta S_m^2. \quad (23)$$

In equations (20) to (23) the subscript  $i$  is used to denote the quantities which are different for the different activities. For example, the effective specific surface free energy for the  $i$ -type active centres is  $\sigma_i$  and it is connected with  $\sigma$  by the relation  $\sigma_i^3 = \Phi_i \sigma^3$ , where the activity factor  $\Phi_i$  is a quantitative measure for the  $i$ -type activity. According to equation (13), a "wetting" angle  $\theta_i$  would correspond to  $\Phi_i$  for  $i$ -type active centres.

If the concentration  $N_{a,i} \text{ (m}^{-3}\text{)}$  of the  $i$ -type active centres is proportional to the concentration  $C \text{ (g m}^{-3}\text{)}$  of the aerosol seeds, we can write

$$N_{a,i} = p_i C, \quad (24)$$

where the unknown factor  $p_i \text{ (g}^{-1}\text{)}$  shows how many  $i$ -type active centres are introduced into the water droplets by seeding them with 1 g of aerosol dust.

Hence, under the simultaneous action of the active centres present initially in the unseeded droplets and of those introduced in the droplets upon seeding them with atmospheric aerosols, the nucleation rate will be

$$J(T) = A_o \exp(-B_o/T^3 \Delta T^2) + \sum_i A_i \exp(-B_i/T^3 \Delta T^2). \quad (25)$$

Using equation (24) in equation (22), and taking into account equation (17) and the fact that practically  $z_i \approx z_o$  and  $n_{s,i}^* \approx n_{s,o}^*$ , to a good approximation we find that

$$A_i = (A_o/N_{a,o}) p_i C. \quad (26)$$



Equation (26) shows that  $A_i$  increases linearly with  $C$ , which means that the nucleation rate  $J_i$  on the  $i$ -type active centres also increases linearly with increasing concentration of aerosol seeds in the droplets [see equation (21)]. According to equation (25), also linear with  $C$  is the change of the overall nucleation rate  $J$  for the droplets seeded with atmospheric aerosols.

The experimentally obtained temperature dependence of  $J$  can be plotted in  $\ln J$  vs  $1/T^3 \Delta T^2$  coordinates. According to equation (25), the presence of well-manifested linear portions in the plot indicates a predominant role of centres of a given type of activity. As  $A_0$  and  $B_0$  are known from experiments with unseeded droplets, the unknown parameters  $A_i$  and  $B_i$  can be estimated by fitting equation (25) to the experimental  $J(T)$  dependence. Using  $B_i$ , one can calculate the values of  $\sigma_i$ ,  $\Phi_i$ ,  $\theta_i$ ,  $n_i^*$  and  $W_i^*$  for the  $i$ -type active centres. Moreover, seeded droplet experiments carried out at different concentrations of aerosol dust make it possible to verify the linear dependence of  $A_i$  on  $C$ , equation (26).

## 6.2. Analysis of the experimental data

The freezing of a population of water droplets seeded with atmospheric aerosols was investigated in three series each comprising four to eight experiments. The weight concentration of aerosol particles in the successive series was  $C = 0.1, 1$  and  $10 \text{ mg cm}^{-3}$ . In each of the series, the total number  $N(T)$  of frozen droplets and the total initial number  $N_0$  of the droplets in the series was determined,  $N_0$  being 396, 789 and 765, respectively, at the above aerosol concentrations. The good reproducibility of the experimental  $N(T)$  dependencies during the time of the experiment (starting 0.5 to 6 h after the preparation of the water-dust suspension for each series) shows that the nucleation activity of the seeds remains unchanged. This implies that no significant seed deactivation due to various physicochemical processes in the suspension takes place during the experimental time.

The experimentally obtained dependence of  $\ln(1 - N/N_0)$  on  $T$  is shown in Fig. 1 by squares, triangles and diamonds for  $C = 0.1, 1$  and  $10 \text{ mg cm}^{-3}$ , respectively. The dependence of  $\ln(1 - N/N_0)$  on  $T$  is determined by the method of smooth approximation of experimental data (see Appendix B) and is illustrated by the curves in Fig. 1. The derivative of the so-obtained temperature dependence of  $\ln(1 - N/N_0)$  and the  $q/v$ -value from Section 4 were used in equation (4) for calculating the nucleation rate  $J(T)$  of ice in seeded water droplets. The resulting  $J(T)$  dependence drawn in  $\ln J$  vs  $1/T^3 \Delta T^2$  coordinates is shown in Fig. 2 by squares, triangles and diamonds corresponding to  $C = 0.1, 1$  and  $10 \text{ mg cm}^{-3}$  (as indicated). Equation (25) was employed to fit the experimental data for all aerosol concentrations upon assuming that active centres of three types of activities,  $i = 1, 2$  and  $3$ , are present on the surface of the aerosol seeds. The obtained best-fit values of the parameters  $A_i$  and  $B_i$  are presented in Table 1. The  $J(T)$  dependence for  $C = 0.1, 1$  and  $10 \text{ mg cm}^{-3}$ , calculated from equation (25) with the  $A_i$  and  $B_i$  values from Table 1, is shown by the curves in Fig. 2. As indicated in the figure, the active centres of type  $i = 1$  and  $3$  dominate, respectively, at the low and high temperature ends of the studied range of temperature, while those of type  $i = 2$  play a role only in the middle of this range. It should be noted that assuming the presence of new active centres of only two types of activities,  $i = 1$  and  $2$ , does not result in good enough fit in the middle of the experimental  $J(T)$  data. Obviously, including more than three types of activities in the fitting procedure (e.g.  $i = 1, 2, 3$  and  $4$ ) will improve the quality of the best fit. In this sense, our choice of three types of activities is not unique, but seems to be the optimal one with respect to the number of fitting parameters and the quality of the fit.

In the same way as in Section 5.2, we determined the parameters  $\sigma_i$ ,  $\Phi_i$ ,  $\theta_i$  and the quantities  $\Delta\mu$ ,  $W_i^*$  and  $n_i^*$  characterizing the activity of the assumed three new types of aerosol-introduced active centres and the process of ice nucleation in the seeded water droplets. The results are given in Tables 2 and 3. The quantities in Table 3 are calculated for the ends of the temperature intervals in which the respective types of active centres play a significant role. It is important to note that the limited knowledge of the physicochemical characteristics of the seeds used does not allow the obtained values of the activity para-

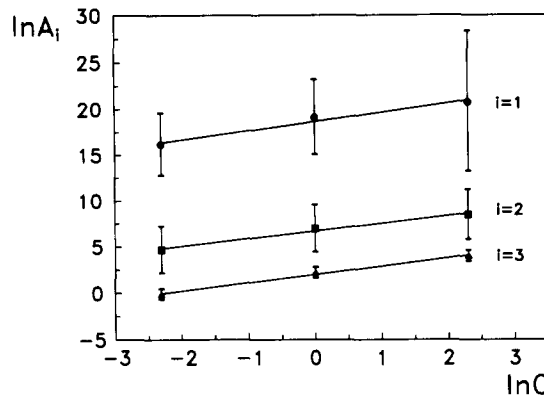


Fig. 3. Dependence of the kinetic factor  $A_i$  ( $\text{cm}^{-3} \text{s}^{-1}$ ) on the concentration  $C$  ( $\text{mg cm}^{-3}$ ) of aerosol seeds: symbols—experimental data, lines—equations (28) to (30).

meters to be attributed to specific properties of the seeds. On the one hand, this makes it impossible to compare these values with those of other investigators. On the other hand, however, it becomes clear that the present method of analysing enables the nucleation activity of the seeds to be characterized quantitatively despite the fact that the nature of the active centres on them is unknown.

The  $A_i$  data from Table 1 can be used for analysing the theoretical dependence of  $A_i$  on  $C$ . According to equation (26), in log-log coordinates the following linear dependence holds for each of the activities  $i = 1, 2$  and  $3$ :

$$\ln A_i = \ln C + \ln(p_i A_o / N_{a,o}). \quad (27)$$

The symbols in Fig. 3 represent the experimental  $A_i(C)$  data from Table 1, and the lines are the best-fit straight lines corresponding to equation (27). These straight lines are described by the following equations ( $C$  is in  $\text{g cm}^{-3}$  and  $A_i$  is in  $\text{cm}^{-3} \text{s}^{-1}$ ):

$$\ln A_1 = (1.0 \pm 0.2) \times \ln C + (18.6 \pm 0.3), \quad (28)$$

$$\ln A_2 = (0.8 \pm 0.1) \times \ln C + (6.7 \pm 0.2), \quad (29)$$

$$\ln A_3 = (0.9 \pm 0.1) \times \ln C + (2.0 \pm 0.1). \quad (30)$$

As seen, the slope of the above straight lines is close to the theoretical slope of 1 in equation (27) and is, thus, in support of the linear dependence (26) of  $A_i$  on  $C$ . With the  $A_o$  value from Table 1, since the above intercepts equal  $\ln(p_i A_o / N_{a,o})$  in equation (27), it follows that  $p_1 = 32 N_{a,o} \text{ cm}^3 \text{ g}^{-1}$ ,  $p_2 = 2.1 \times 10^{-4} N_{a,o} \text{ cm}^3 \text{ g}^{-1}$  and  $p_3 = 1.9 \times 10^{-6} N_{a,o} \text{ cm}^3 \text{ g}^{-1}$ .

Using these findings for  $p_i$  in equation (24) leads to the conclusion that, for instance, at  $C = 0.1 \text{ mg cm}^{-3}$  the ratio between the aerosol-introduced and the initially present active centres is  $N_{a,1}/N_{a,o} = 3.2 \times 10^{-3}$ ,  $N_{a,2}/N_{a,o} = 2.1 \times 10^{-8}$  and  $N_{a,3}/N_{a,o} = 1.9 \times 10^{-10}$ . From here it follows also that  $N_{a,2}/N_{a,1} = 7 \times 10^{-6}$  and  $N_{a,3}/N_{a,1} = 6 \times 10^{-8}$ .

These numbers are quite understandable upon recalling that the aerosol-introduced active centres of type 1 are less active than those of type 2 which, in turn, are less active than those of type 3 (see the  $\Phi_i$  values in Table 2).

## 7. CONCLUSION

The experiments carried out show that reliable data for the nucleation of crystals in melts can be obtained from the temperature dependence of the number of the unfrozen droplets of an ensemble. The method proposed for analysing the kinetics of droplet freezing during undercooling at constant rate makes it possible to determine the nucleation rate  $J$ . This quantity is obtained in general form from the temperature derivative of the logarithm of the relative number of unfrozen droplets.

The analysis made shows that the obtained experimental data can be described in terms of the classical nucleation theory. In the investigated temperature interval ice nucleation in unseeded distilled water is heterogeneous and is controlled by only one type of active centre. Upon seeding the water with aerosol dust, new active centres are introduced with three types of activities, one of which is close to the activity of the active centres in the unseeded water. The aerosol-introduced active centres and their activities are characterized by effective specific surface energy  $\sigma_{\text{ef}} = 4.1\text{--}10.9 \text{ mJ m}^{-2}$ , activity factor  $\Phi = 0.01\text{--}0.16$  and "wetting" angle  $\theta = 27\text{--}55^\circ$ . The nucleation work is  $W^* = (1\text{--}23) kT$  at  $\Delta\mu = (0.06\text{--}0.22) kT$ . The size of the critical nucleus ( $n^* = 7\text{--}330$ ) is reasonably large from the view point of the classical nucleation theory. The theoretically expected linear dependence of the kinetic factor  $A_i$  on the concentration  $C$  of the aerosol seeds is experimentally confirmed and the relative number of the aerosol-introduced active centres is calculated.

The most informative application of the proposed method for determining and analysing the nucleation rate of crystals in melts is to model systems with well-characterized seeds. The present study shows that this method can also be applied to more complicated systems containing atmospheric pollutants even with unknown physicochemical characteristics. In this case the method provides a formal quantitative description of the activity of these pollutants with respect to crystal nucleation.

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## REFERENCES

- Bashkirova, G. M. and Pershina, T. A. (1965) *Trudy Glav. Geofiz. Observ.* **176**, 35.  
 Bigg, E. K. (1953a) *Proc. Phys. Soc. B* **66**, 688.  
 Bigg, E. K. (1953b) *Q. Jl R. Met. Soc.* **79**, 510.  
 Bilkova, E., Dubrovski, M., Petera, W. and Skoloud, O. (1989) *Trudy Tzentral. Aerolog. Observ.* **174**, 11.  
 Boucher, E. A. (1969) *Nucleation* (Edited by Zettlemoyer, A. C.), p. 527. Dekker, New York.  
 Butorin, G. T. and Skripov, W. P. (1972) *Kristallografiya* **17**, 379.  
 Clause, D. (1985) *Encyclopedia of Emulsion Technology* (Edited by Becher, P.), Vol. 2, p. 77. Dekker, New York.  
 Clause, D., Dumas, J. P., Meyer, P. H. E. and Broto, F. (1987) *J. Dispersion Sci. Technol.* **8**, 1.  
 Clause, D., Kashchiev, D. and Jolivet, C. (1990) *Entropie* **153/154**, 33.  
 Dubrovski, M. and Skoloud, O. (1988) *Atmospheric Aerosols and Nucleation* (Edited by Wagner, P. E. and Valy, G.). Springer, Berlin.  
 Dubrovski, M. and Skoloud, O. (1989) *Studia Geophys. Geodes.* **33**, 287.  
 Genadiev, N. (1970) *J. Rech. Atmos.* **4**, 81.  
 Gutzw, I., Kashchiev, D. and Avramov, I. (1985) *J. Non-Cryst. Solids* **73**, 477.  
 Huige, N. J. J. and Thijssen, H. A. C. (1969) *Proc. Symp. Industrial Crystallization*, London, p. 69.  
 Kashchiev, D. (1969) *Surf. Sci.* **14**, 209.  
 Kashchiev, D. (1970) *Surf. Sci.* **22**, 319.  
 Kashchiev, D. (1984) *Cryst. Res. Technol.* **19**, 1413.  
 Kashchiev, D., Clause, D. and Jolivet-Dalmazzone, C. (1994) *J. Colloid Interface Sci.* **165**, 148.  
 Kashchiev, D., Verdoes, D. and van Rosmalen, G. M. (1991) *J. Crystal Growth* **110**, 373.  
 Kozisek, Z. (1990) *Czech. J. Phys. B* **40**, 592.  
 Kozisek, Z. and Chvoj, Z. (1989) *Czech. J. Phys. B* **39**, 1.  
 Kупенова, T. (1980) Commun. JINR, Dubna P11-80-669.  
 Kупенова, T. and Stoyanova, V. (1993) *Physics Computing '92* (Edited by de Groot, R. A. and Nadrchal, J.), p. 386. World Scientific, Singapore.  
 Macklin, W. C. and Ryan, B. F. (1966) *Phil. Mag.* **14**, 847.  
 Macklin, W. C. and Ryan, B. F. (1968) *Phil. Mag.* **17**, 83.  
 Mason, B. J. (1957) *The Physics of Clouds*. Clarendon, Oxford.  
 Rasmussen, D. H. and MacKenzie, A. P. (1971) *Water Structure at the Water-Polymer Interface* (Edited by Jellinek, H. H. G.), p. 126. Plenum, New York.  
 Spengler, J. D. and Gokhale, N. R. (1972) *J. appl. Meteorol.* **11**, 1101.  
 Talmi, A. and Gilat, G. (1977) *J. Comp. Phys.* **23**, 93.  
 Toner, M. and Gravalho, E. G. (1990) *J. appl. Phys.* **67**, 1582.  
 Toshev, S. (1973) *Crystal Growth: an Introduction* (Edited by Hartman, P.), p. 1. North-Holland, Amsterdam.  
 Toshev, S., Milchev, A. and Stoyanov, S. (1972) *J. Crystal Growth* **13/14**, 123.  
 Valy, G. (1985) *J. Rech. Atmos.* **19**, 105.

- van der Leeden, M. C., Kashchiev, D. and van Rosmalen, G. M. (1993) *J. Crystal Growth* **130**, 221.  
 Volmer, M. (1939) *Kinetik der Phasenbildung*. Steinkopff, Dresden.  
 Walton, A. G. (1969) *Nucleation* (Edited by Zettlemoyer, A. C.), p. 225. Dekker, New York.

## APPENDIX A

Let us verify if the obtained  $J$  values in Fig. 2 satisfy the criterion for operativeness of the mononuclear mechanism of crystallization. As known (e.g. Kashchiev *et al.*, 1991), this mechanism is operative when the time  $t_1$  for the appearance of the first crystal nucleus in the system is much longer than the time  $t_G$  for the complete crystallization of the melt, i.e. when  $t_1 \gg t_G$ . In steady-state nucleation  $t_1$  is given by  $t_1 = 1/Jv$  (Toshev *et al.*, 1972). The time  $t_G$  depends on the drop radius  $R$  and the crystal growth rate  $G$  [ $\text{m s}^{-1}$ ]. At time-independent  $G$ ,  $t_G = R/G$ , where  $R = (3v/4\pi)^{1/3}$ . As a result, for the mononuclear mechanism to be operative it is necessary that (Kashchiev *et al.*, 1991)

$$(4\pi/3)^{1/4} (G/J)^{3/4} / v > 1. \quad (31)$$

In the present experiments the mean volume of one water droplet from the population is  $v = 10^{-3} \text{ cm}^{-3}$ , and the maximum value of  $J$  is  $10^3 \text{ cm}^{-3} \text{ s}^{-1}$  (see Fig. 2). This  $J$  value is most unfavourable for the operativeness of the mononuclear mechanism and would result in the formation of  $Jvt_{\text{exp}} \approx 200\text{--}500$  nuclei in a droplet during the time  $t_{\text{exp}} = 3\text{--}8$  min of the experiment if nucleus overgrowth were not fast enough.

From the literature (Macklin and Ryan, 1966, 1968; Huige and Thijssen, 1969) the value of  $G$  is known to be about  $1\text{--}4 \text{ cm s}^{-1}$  at  $\Delta T = 10 \text{ K}$ . Again, the most unfavourable value of the ice growth rate of  $1 \text{ cm s}^{-1}$  is taken for the evaluation of the criterion (31). With the above values of  $v$ ,  $J$  and  $G$ , it follows that the left-hand side of (31) is about 10. Hence, the obtained  $J(T)$  data are consistent with the supposition that the mononuclear mechanism is operative in the experiments carried out.

## APPENDIX B

The problem of data approximation can be formulated in the following way: given the error-containing values  $F(x_i)$  of a function  $F(x)$  ( $x_i \in [a, b]$ ,  $i = 1, \dots, N$ ), it is required to restore the function in the whole interval  $[a, b]$  and also to find its derivatives.

The method of smooth approximation of data (Talmi and Gilat, 1977; Kупенова, 1980; Kупенова and Stoyanova, 1992) is based on the choice of the smoothest analytical function  $g(x)$  that passes as close as possible to the data points. In order to fulfil this, a criterion for smoothness of the approximating analytical function  $g(x)$  is introduced in the following way: let the function  $g(x)$  and its derivatives be defined and finite in the interval  $[a, b]$ . It is possible to construct a norm  $I(g)$  which includes all the derivatives of  $g(x)$  and is required to be minimum:

$$I(g) = \sum_{n=1}^{\infty} B_n \int_a^b |g^{(n)}(x)|^2 dx = \min.$$

The constants  $B_n$  are introduced to ensure the convergence of the series.

The two contradictory requirements for proximity to the data and smoothness of  $g(x)$  can be combined into the following single condition for minimizing the functional:

$$\sum_{i=1}^N |F(x_i) - g(x_i)|^2 \omega_i + \omega_0 I(g) = \min,$$

where  $\omega_i$  is the weight of the  $i$ th data point and  $\omega_0$  is a parameter of smoothing. It is appropriate to choose  $\omega_i$  in conjunction with the experimental error  $\sigma(x_i)$ , namely  $\omega_i = [\sigma(x_i)]^{-2}$ . The choice of  $\omega_0$  is very important. While exceedingly small  $\omega_0$  can lead to the appearance of oscillations in  $g(x)$ , too large  $\omega_0$  may result in smooth  $g(x)$ , but quite away from the data. In the absence of any additional information the optimal  $\omega_0$  can be determined by varying it until the first term of the above functional becomes close to  $N$ :

$$\sum_{i=1}^N |F(x_i) - g(x_i)|^2 \omega_i \approx N.$$

It can be proved that this problem has a single solution in the form

$$g(x) = \sum_{j=1}^N \lambda_j R(x, x_j),$$

where  $R(x, y)$  is a known function, and the constants  $\lambda_j$  are determined by solving the following set of linear equations ( $i = 1, \dots, N$ ):

$$g(x_i) = \sum_{j=1}^N \lambda_j R(x_j, x_i) = F(x_i).$$

It can be shown that the error  $t(x) = F(x) - g(x)$  is limited from above by a value which decreases exponentially with increasing  $N$ . A similar limit exists also for the derivatives of  $F(x)$ , and this makes the method good for finding these derivatives, too.

The main advantages of this method are good approximation for the function and its derivatives, absence of oscillations between neighbouring data points and reduction of the noise level.