Heterogeneous Drop Freezing in the Immersion Mode: Model Calculations Considering Soluble and Insoluble Particles in the Drops

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ABSTRACT

A method is presented to consider the influence of both soluble and insoluble aerosol particles on drop freezing in the immersion mode in cloud models. Most atmospheric aerosol particles contain soluble and insoluble materials. Thus, a more realistic description of drop freezing should account for both factors. In general, salt particles depress the freezing point according to the salt concentration, while insoluble particles raise the freezing temperature. Based on laboratory experiments, a semiempirical equation was derived to calculate the median freezing temperature as a function of the drop size and for different insoluble particles. The freezing point depression was determined using the activity coefficients of the salt solutions. The results obtained with the freezing model for drops containing soluble and insoluble particles are consistent with experimental results. An equation for the freezing rate was derived and incorporated into an adiabatic air parcel model with detailed sectional microphysics. Model simulations were carried out to compare the present approach to the Bigg approach for drop freezing, which is often employed in cloud models. The results indicated that the Bigg equation describes drop freezing well in the immersion mode for a "mean" insoluble particle; however, the presented equations consider the significantly different freezing characteristics of various ice nuclei. Therefore, drop freezing in the immersion mode can be described for defined aerosol particle distributions as a function of the fractions of the different insoluble particles to the total aerosol particles.

1. Introduction

Field measurements in tropospheric clouds showed that supercooled liquid water drops and frozen drops can coexist at very low temperatures down to −40°C (e.g., Heymsfield and Sabin 1989; Heymsfield and Miloshevich 1993) with an incidence of ice particles already at rather warm temperatures of −4°C (e.g., Mossop et al. 1970; Hobbs et al. 1974). Homogeneous freezing of solution drops formed on soluble cloud condensation nuclei will not play an important role at temperatures above −35°C (e.g., Hagen et al. 1981; Sassen and Dodd 1988; Jensen et al. 1998; Koop et al. 1999). Therefore, the distribution of supercooled liquid water drops and frozen drops in tropospheric clouds may be influenced by heterogeneous ice nucleation due to insoluble or mixed aerosol particles at all temperatures below 0°C. That this mechanism takes place in the atmosphere was verified by the chemical identification of aerosol particles found in the center of ice crystals (e.g., Kumai and Francis 1962; Kikuchi et al. 1982). A diversity of field measurements was undertaken to investigate atmospheric ice nuclei, their concentrations, size distributions and chemical compositions (for a review, see Pruppacher and Klett 1997). Furthermore, a large number of laboratory experiments was carried out to study the ice nucleating ability of various aerosol particles (e.g., Fukuta 1958; Roberts and Hallett 1968; Schnell and Vali 1976; Vali et al. 1976; Schaller and Fukuta 1979; Al-Naimi and Saunders 1985; Gorbunov et al. 2001) accompanied by numerical investigations and discussions about the role of heterogeneous freezing nucleation in the atmosphere (e.g., Young 1974; Vali 1985; DeMott et al. 1997, 1998).

One primary freezing process taking place in the atmosphere is immersion freezing where water drops are formed prior to cooling and afterward supercooled until they reach a critical temperature where they start freezing (Pruppacher and Klett 1997). The determining factors for this critical temperature are the volume of the drop, the concentration of salts in the drop, the content of insoluble particles in the drop and their size. Field measurements showed that most mixed aerosol particles contain an insoluble fraction of between 12% and 90% (e.g., Winkler 1974; Svenningson et al. 1994; Eichel et al. 1996). The heterogeneous mixture (soluble and insoluble fractions) of atmospheric aerosol particles leads to the formation of equal-sized drops with different compositions in a cloud and, therefore, to different freezing temperatures of equal-sized drops.

The influence of insoluble particles, that is, ice for-

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TABLE 1. Median freezing temperatures for drops of various sizes containing different insoluble particles according to laboratory experiments.

Drop radius	≈50 μm	≈250 μm	≈350 μm
Pure water drops (Mason 1957)	−35°C	−34°C	−33°C
Soot particles			
From acetylene	for $a < 15$ μm: < -34°C (DeMott 1990)		
From kerosene			−28°C (Diehl and Mitra 1998)
Mineral particles			
Kaolinite	−32.5°C (Hoffer 1961)		−23°C (Pitter and Pruppacher 1973)
Montmorillonite	−24.0°C (Hoffer 1961)		−19°C (Pitter and Pruppacher 1973)
Illite	−23.5°C (Hoffer 1961)		
Biological particles			
Pollen		−14°C (Diehl et al. 2002)	
Leaf litter			−9°C (Diehl et al. 2001)
Bacteria		−7°C (Levin and Yankofski 1983)	

mation by heterogeneous freezing, was described in model calculations by, for example, Meyers et al. (1992), Vali (1994), and Khvorostyanov and Curry (2000). Immersion freezing was considered in many model studies (see reviews in Pruppacher and Klett 1997; Khain et al. 2000). DeMott et al. (1994) studied immersion freezing for particles containing soluble and insoluble components. However, none of these parameterizations considered the actual amount, nor the different freezing characteristics of soluble and insoluble materials inside the drops.

This encouraged the authors to conduct model investigations of the influence of soluble and insoluble particles on water drop freezing. A possible increase of the freezing temperatures due to the content of insoluble particles acting as ice nuclei was implemented based on laboratory investigations. A two component description according to Wurzler and Bott (2000) was employed to study the freezing point depression as a function of the salt concentration in the drop. To show the benefits of the presented heterogeneous freezing approach, it was incorporated into an air parcel model with detailed sectional microphysics including the ice phase. The results obtained with the presented freezing approach were compared to those obtained with the Bigg approach for ice formation via drop freezing.

2. Methods

a. Freezing temperatures due to insoluble particles

The freezing temperature of the drops was described by the median freezing temperature because this illustrates well the freezing efficiency of insoluble particles. It is defined as the temperature where 50% of an observed monodispersed drop population freezes. A disadvantage of using the median freezing temperature may be that the first initiation of ice nucleation that could be critically important in some cases is not resolved.

To provide an experimental basis for the model calculations, laboratory studies were selected dealing with the freezing process of drops owing to immersion freezing as a function of drop size. The influence of the particle size on drop freezing was shown experimentally by, for example, Gerber (1976), DeMott (1990), and Gorbunov et al. (2001). However, laboratory studies where the freezing dependence on the particle size was investigated in terms of the median freezing temperature could not be found in literature. Thus, potential particle size effects on drop freezing were neglected in the present study. In Table 1, median freezing temperatures found in the literature are listed for drops of different drop sizes. The smaller the drop size, the lower is the freezing temperature. This correlation holds not only for pure water drops (Mason 1957), but also for drops containing insoluble particles and is a result of the stochastic nature of the formation of ice germs (Pruppacher and Klett 1997). Well-known atmospheric immersion freezing nuclei lead to an increase of the freezing temperature: soot particles (DeMott 1990; Diehl and Mitra 1998) only slightly increase the freezing temperature, while mineral particles (Hoffer 1961; Pitter and Pruppacher 1973) and especially biological particles (Levin and Yankofski 1983; Diehl et al. 2001, 2002) significantly increase the freezing temperature. All these insoluble particles are present in the atmosphere and were detected during several investigations (for a review see Pruppacher and Klett 1997). Sources are anthropogenic combustion processes for soot particles; the earth's surface for mineral particles; and plants, decaying vegetation, and vegetation fires for biological particles.

Two assumptions were made to incorporate the freezing temperatures of drops containing insoluble particles into the model studies. First, the freezing temperature was assumed to be independent of the size of the insoluble particles. Following the suggestions of several authors (e.g., Levine 1950; Bigg 1953; Langham and Mason 1958; Vali 1971), it was further assumed that the median freezing temperature is a function of the logarithm of the drop volume that can be expressed by the following equation (Pruppacher and Klett 1997):

$$-T_m = A - B \ln V_d, \quad (1)$$

where T_m is the median freezing temperature, V_d is the drop volume, and A and B are constants. This correlation has been verified in various experiments by the above-cited and other authors (see Pruppacher and Klett 1997).

Two different points of view exist (Puppacher and Klett 1997) to explain the freezing behavior of water drops containing insoluble particles. According to the stochastic hypothesis (e.g., Bigg 1953), the formation of ice germs inside a supercooled water drop depends on random nucleation. Insoluble particles enhance the efficiency of the random nucleation but do not disturb its stochastic nature. The median freezing temperature according to the stochastic hypothesis can be calculated similarly as in. Eq. (1) (see Pruppacher and Klett 1997):

$$-T_m = \frac{1}{a} \ln \frac{a \ln 2 \ln \gamma}{b} - \frac{1}{a} \ln V_d, \quad (2)$$

with γ a fixed cooling rate, and a and b constants. According to the singular hypothesis (e.g., Levine 1950; Langham and Mason 1958), the number of ice germs formed in a supercooled water drop is dependent on the number of ice nuclei active in a defined temperature range. The median freezing temperature for this hypothesis can be calculated similarly as in. Eq. (1) (see Pruppacher and Klett 1997):

$$-T_m = \frac{1}{c} \ln \frac{\ln 2}{n_{p,0}} - \frac{1}{d} \ln V_d, \quad (3)$$

with $n_{p,0}$ the number density of particles inside the drop, and c and d constants.

To come to a relationship of less complexity, it was assumed that the number of frozen drops was independent 1) of the cooling rate and 2) of the number density of particles in the drop. The following semiempirical relationship was derived:

$$-T_m = \frac{1}{a} \ln \frac{\ln 2}{B_{h,i}} - \frac{1}{a} \ln V_d, \quad (4)$$

with the constants a and $B_{h,i}$. In Eqs. (1)–(4), the temperature is in degrees Celsius, and the drop volume V_d is in cubic centimeters. In Eq. (4), the constant a is in reciprocal degrees Celsius, and the constant $B_{h,i}$ is per cubic centimeter. The constant $B_{h,i}$ stands for the ice nucleating efficiency in the immersion freezing mode of an insoluble particle per unit volume of liquid. The more efficiently a particle can act as an immersion freezing nucleus, the higher is the value for $B_{h,i}$. The values for $B_{h,i}$ were derived from experimental results for the above-mentioned soot particles (Diehl and Mitra 1998), mineral particles (Hoffer 1961; Pitter and Pruppacher 1973), and biological particles (Levin and Yankofski 1983; Diehl et al. 2001, 2002). Values between 1×10^{-9} cm^{-3} and 10 cm^{-3} were found. The data for all investigated particles are listed in Table 2.

Table 2. Values of $B_{h,i}$ for various insoluble particles derived from laboratory experiments.

Type of particle	$B_{h,i}$ (cm^{-3})
Soot particles	
From kerosene	2.91×10^{-9}
Mineral particles	
Kaolinite	6.15×10^{-8}
Montmorillonite	3.23×10^{-5}
Illite	6.19×10^{-5}
Biological particles	
Pollen	1.01×10^{-2}
Leaf litter	4.38×10^{-1}
Bacteria	6.19

The semiempirical form of Eq. (4) that is based on laboratory results, was preferred because a derivation from thermodynamics would not be able to describe all the complex freezing properties of an ice nucleus, such as the number and characteristics of the ice active sites on the particle. Equation (4) permits calculation of the median freezing temperature of drops depending only on their volume and the knowledge of the kind as insoluble particles involved.

b. *Freezing point depression*

The content of soluble salts in a drop leads to a freezing point depression due to the salt concentration in the drop (e.g., Hoffer 1961; Bertram et al. 2000; Möhler et al. 2003). This freezing point depression was determined with the approach of Koop et al. (2000). Based on laboratory experiments they showed that the freezing of supercooled aqueous solution drops depends only on the water activity of the solution. Using their parameterization of the water activity criterion for homogeneous ice nucleation, the freezing temperatures of pure water $T_{f,0}$ and of solutions $T_{f,s}$ were calculated. The freezing temperature of pure water was calculated with an activity coefficient of 1. The freezing temperatures of solutions with different salt concentrations were calculated with the corresponding values of the activity coefficients. These were found in Pruppacher and Klett (1997) for ammonium sulfate and sodium chloride. The freezing temperatures were calculated under the assumption that freezing sets in when the nucleation rate J is larger than 1 cm^{-3} s^{-1}. From these two freezing temperatures, the freezing point depression ΔT_f was obtained by

$$\Delta T_f = T_{f,0} - T_{f,s}. \quad (5)$$

It is to be noted that Koop et al. (2000) found that a large number of different solutes did not lead to a wide spread of freezing temperatures. Thus, the freezing point depressions calculated with their parameterization will be in the same range for different solutions.

It was assumed that the freezing point depression of heterogeneous freezing is the same as for pure solution drops (i.e., homogeneous freezing) which is a simplification of the real case where the homogeneous freezing point depression is somewhat lower than the heterogeneous freezing point depression. However, according to DeMott (2002), who evaluated earlier experimental data, at least the relationship between the freezing point depression and the concentration of the solution for heterogeneous freezing runs parallel to the one for homogeneous freezing.

c. *Two-dimensional description*

To show the effects of different solution concentrations on drop freezing, a two-dimensional size distribution of drops and aerosol particles was used. This was divided into 46 categories for aerosol particles ranging from 1×10^{-2} to 30 μm in radius, and into 64 categories for the drops ranging from 1×10^{-2} to 5×10^{3} μm in radius, with a mass doubling in every other category. For each point in the drop–aerosol particle field, the two effects of immersion freezing caused by insoluble particles and freezing point depression due to soluble particles were combined by adding the value of ΔT_f from Koop's et al. (2000) parameterization to the freezing temperature obtained from equation (4). In this manner, the drop–aerosol particle field for a given temperature was divided into two parts: one part where the drops freeze, and one part where the drops do not freeze. Employing the two-dimensional treatment of cloud physics allows the coexistence of similarly sized drops with different contents of soluble particles, that is, different freezing temperatures (Bott 1999; Trautmann and Wanner 1999; Wurzler and Bott 2000; Reisin and Wurzler 2001).

Two different soluble particles were considered, namely, sodium chloride and ammonium sulfate. For the insoluble particles, besides soot particles and mineral particles kaolinite, montmorillonite, and illite, biological particles pollen, leaf litter, and bacteria were investigated. It is to be noted that the listed mineral particles, as well as the soot particles, cover more or less the whole range of particle sizes used in the present calculation, while biological particles are species with particular sizes. However, even though a part of this size range is not typical for most biological particles, it was included in the present studies.

For a comparison, the homogeneous freezing of pure water and solution drops containing no insoluble particles was also calculated. Based on the results of Mason (1957, see Table 1) a similar constant like $B_{h,i}$ was derived. The value for this constant B_{hom} was 8.347×10^{-10} cm^{-3}. Unfortunately it does not match with Mason's results for drop sizes larger than 100 μm (the calculated freezing temperatures are about 10% higher); however, it is not planned to incorporate this part of homogeneous freezing in cloud models. In the present study, the results should just serve as reference values to prove that heterogeneous freezing takes place at warmer temperatures.

3. Model simulations

The presented approach for drop freezing in the immersion mode was incorporated into an entraining air parcel model with detailed sectional microphysics including the ice phase (Alheit et al. 1990; Respondek et al. 1995). The description of the cloud microphysics is one-dimensional, which implies that similarly sized drops contain similar amounts of aerosol particles. The model was conceived to study the wet removal of atmospheric pollutants from the atmosphere by mixed-phase clouds. It includes many cloud microphysical processes such as nucleation of drops and snow crystals, growth by water vapor diffusion, growth of drops by collision and coalescence, and growth of snow crystals by riming. Drop freezing was described according to Bigg (1953). For the present model simulations, only warm microphysics and drop freezing were included. First a reference run with Bigg's approach was conducted. Then the Bigg equation was replaced by an equation for the freezing rate with the derived $B_{h,i}$ constants for different insoluble particles.

This equation for the freezing rate was derived by an approach for heterogeneous ice nucleation similar to the the approach of Pruppacher and Klett (1997) for homogeneous ice nucleation. It follows a heuristic approach and considers a population of N_0 equal-sized water drops. In the following equations, the temperatures T_m and T are in degrees Celsius. It is assumed that a nucleation event in any drop is independant of that in another drop and that ice formation is the result of only one nucleation event per drop. This implies for the case of heterogeneous freezing that, independent of how many insoluble particles are inside the drop, the one insoluble particle whose active site initiates ice formation leads to drop freezing. The number of ice germs produced in the liquid volume $N_u V_d$ during cooling by dT is given by

$$N_{i,g}(T - dT) - N_{i,g}(T) = N_u V_d J(T) dT, \qquad (6)$$

with $N_{i,g}(T)$ the number of ice germs at temperature T, dT the temperature interval, N_u the number of unfrozen drops, and $J(T)$ the nucleation rate. Note that the units of $J(T)$ are per cubic centimeter degree Celsius.

This equation is time independent, which means, assuming the drop volume does not change with temperature, at any given temperature ice formation happens instantaneously and the number fraction of freezing drops is predetermined by the temperature and the constant $B_{h,i}$. With $dN_u = -dN_f$, where N_f denotes the number of frozen drops, Eq. (6) can be written as

$$\frac{1}{N_u}dN_u = V_d J(T) dT. \tag{7}$$

Integrating this equation leads to

$$\ln\frac{N_0}{N_u} = \int V_d J(T)\, dT. \tag{8}$$

On the other hand, Eq. (4) can be rewritten as

$$\ln 2 = \ln\frac{N_0}{N_u(T_m)} = V_d B_{h,i} \exp(aT_{\text{sm}}) \tag{9}$$

by using the relationship that

$$N_u(T_m) = \frac{N_0}{2}, \tag{10}$$

with N_0 the total number of drops, $N_u(T_m)$ the number of unfrozen drops at the median freezing temperature, $T_{\text{sm}} = T_0 - T_m$, $T_0 = 0°\text{C}$. Therefore, one can deduce from Eqs. (8) and (9) that

$$J(T) \approx aB_{h,i} \exp(aT_s), \tag{11}$$

with $T_s = T_0 - T$, $T_0 = 0°\text{C}$. Using this relationship, one obtains the following equation for the freezing rate from Eq. (7):

$$-\frac{dN_f}{dt} = \frac{dN_u}{dt} = N_u a B_{h,i} V_d \exp(aT_s)\frac{dT}{dt}, \tag{12}$$

which is the freezing rate for pure water drops of same sizes containing insoluble particles.

Drop freezing in the model simulations was treated as if all insoluble material consists of one species to demonstrate their specific effects. Solution effects were added as described above. As an initial condition, a background aerosol particle size distribution was chosen from Jaenicke (1988) with a mass fraction of 50% soluble material (ammonium sulfate in the present case). The vertical temperature and humidity distribution, which the air parcel passed through, was that measured at the Rhein–Main area, Germany, on 27 June 1988 at 1300 (local time).

4. Results and discussion

a. Freezing point depression

The model results for the freezing temperatures $T_{f,s}$ of drops containing ammonium sulfate, as well as the freezing point depression ΔT_f, are listed in Table 3 together with the experimental values for homogeneous freezing of solution drops from Bertram et al. (2000), which were part of the basis of the Koop et al. (2000) parameterization. The drops Bertram et al. (2000) used in their experiments had a mean radius of 16 μm. The freezing temperatures given in Table 3 were calculated with a polynominal equation given by Bertram et al. (2000). Because of the sectional distribution of aerosol particles and drops into size classes, only discrete values for the salt concentrations are available from the present model calculations for drop freezing. These salt concentrations are given in Table 3 in percent weight. The freezing temperature of drops of 16-μm radius containing ammonium sulfate was calculated with the present model as follows: according to Eq. (4) the freezing temperature of the drop due to its size was calculated using the constant B_{hom} as given in section 2c. Afterward, the freezing point depression due to the ammonium sulfate concentration in the drop was added to this value.

Table 3. Comparison of model results to experimental results concerning the freezing point depression of solution drops of 16-μm radius (Bertram et al. 2000) for different ammonium sulfate concentrations: freezing temperature is T_f and freezing point depression is ΔT_f.

Concentration (weight %)	Bertram's experimental results T_f (°C)	ΔT_f (°C)	Model results T_f (°C)	ΔT_f (°C)
0	−38.0	0	−38.42	0
0.102	−38.07	−0.07	−38.47	−0.05
0.204	−38.14	−0.14	−38.53	−0.11
0.408	−38.29	−0.29	−38.65	−0.23
0.813	−38.57	−0.57	−38.80	−0.38
1.612	−39.13	−1.13	−39.45	−1.03
3.173	−40.16	−2.16	−40.33	−1.91
6.152	−42.07	−4.07	−41.22	−2.80
11.591	−45.36	−7.36	−43.80	−5.38
20.775	−51.21	−13.21	−47.73	−9.31
34.402	−66.42	−28.42	−64.60	−26.18

As one can see from Table 3 the model results for ammonium sulfate agree well with the experimental results from Bertram et al. (2000) indicating that the parameterization was correctly implemented into the present model.

b. Frozen and liquid drop size distributions

In Figs. 1 and 2, frozen and liquid size distributions are given as results of model calculations with the two-dimensional drop–aerosol particle field for two different temperatures. Drop sizes range from 0.01- to 5000-μm radius, aerosol particle sizes from 0.01- to 30-μm radius. Please note that aerosol particle size in these diagrams stands for the equivalent radius of the soluble mass fraction of the aerosol particles inside the drops for the cases including freezing point depression. In these cases, the insoluble particle has an arbitrary size. For the cases regarding pure water drops, the x axis indicates the size of the insoluble particles. The light gray field in the right lower corner represents what is not physically possible because the particle size cannot be larger than the drop size. The lines mark the threshold between the drops that can freeze and the drops that cannot freeze. Solid lines represent results for pure water drops, dotted lines results for salt solution drops. The insoluble particles are labeled in the diagrams. The salt concentrations in the drops are determined by the relation between drop radius and the equivalent radius of the soluble mass

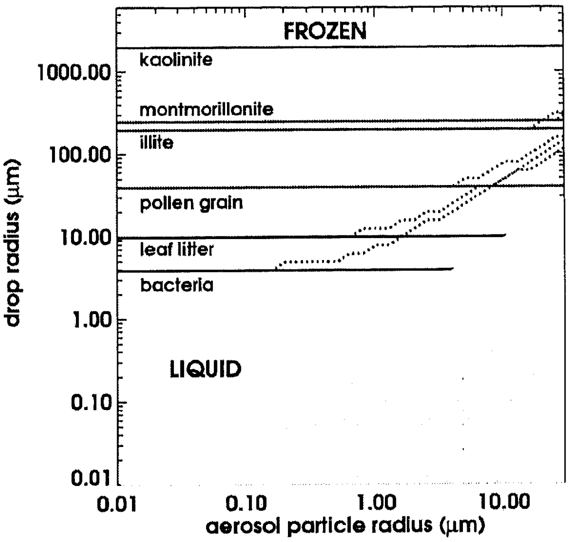

FIG. 1. Distribution of supercooled liquid water drops and frozen drops in a two-dimensional field of drops and aerosol particles with given radii at a temperature of −20°C. Drops contain ammonium sulfate as soluble particles and various insoluble particles.

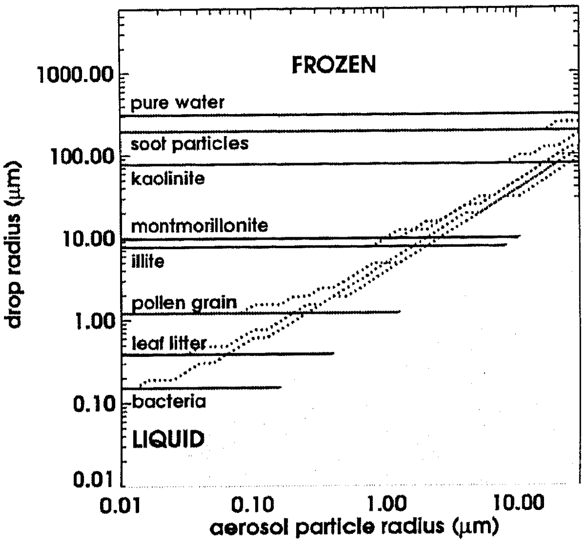

FIG. 2. As in Fig. 1 for a temperature of −30°C.

fraction of the particle. For the calculations represented in Figs. 1 and 2, ammonium sulfate was selected as the soluble particle mass fraction.

Figure 1 represents the model results at −20°C, Fig. 2 at −30°C. One can notice from both figures that the insoluble particles affect the freezing of drops of significantly different sizes. At −20°C, biological particles initiate the freezing of rather small drops with sizes between 5 and 50 μm in radius and larger. Water drops containing mineral particles cannot freeze unless they have rather large radii of more than 100 μm. At −30°C, pure water drops and solution drops with radii around 500 μm can be expected to freeze. Nearly the same is the case for drops containing soot particles, while biological and mineral particles affect the freezing of drops with sizes between 10 and 100 μm and larger and between 0.1 and 1 μm and larger, respectively. One can further notice that these thresholds do not change for solution drops containing the insoluble particles as long as the salt concentration stays below a critical value, that is, less than 1×10^{-3} mol L^{-1}. For higher concentrated salt solution drops, the freezing is shifted to larger drop sizes. This threshold value was also found by Pruppacher and Neiburger (1963) in laboratory experiments.

Table 4 shows a comparison of model-calculated freezing temperatures of solution drops containing mineral particles to the experimental values of Zuberi et al. (2002). They studied the freezing of ammonium sulfate solution drops containing kaolinite and montmorillonite particles. The sizes of the drops were between 10 and 55 μm, the model results were calculated for a mean drop radius. The results for kaolinite and montmorillonite were summarized in Zuberi et al. (2002). As one can see from Table 4, the freezing temperatures of Zuberi et al. (2002) for both mineral particles lie between the model results for kaolinite and montmorillonite.

The model results indicate that homogeneous freezing is rather unimportant at temperatures warmer than −35°C and that, in the temperature range relevant for the troposphere, the composition of the drops has an important influence on their freezing behavior in the immersion mode. The lower the temperatures, the stronger are the effects of insoluble particles on smaller drop sizes. The smaller the drop sizes, the greater is the effect of the mass fractions of the soluble particles. For these cases the advantage of the two-dimensional description becomes evident: equal sized drops are allowed to contain soluble aerosol particles of different sizes and, thus, do not freeze at the same temperature.

c. Results of model simulations

Results of the model simulation with the air parcel model as described in section 3 are shown in Fig. 3.

TABLE 4. Comparison of model results to experimental results of Zuberi et al. (2002) for the freezing temperatures of ammonium sulfate solution drops containing insoluble mineral (kaolinite and montmorillonite) particles.

Concentration ($g\ L^{-1}$)	Zuberi's experimental results	Model results	
	Both minerals	Kaolinite	Montmorillonite
	Freezing temperature T_f (°C)		
60	−33	−37.0	−30.8
120	−35	−39.6	−33.3
260	−42	−43.5	−37.3
530	−55	−60.2	−54.0

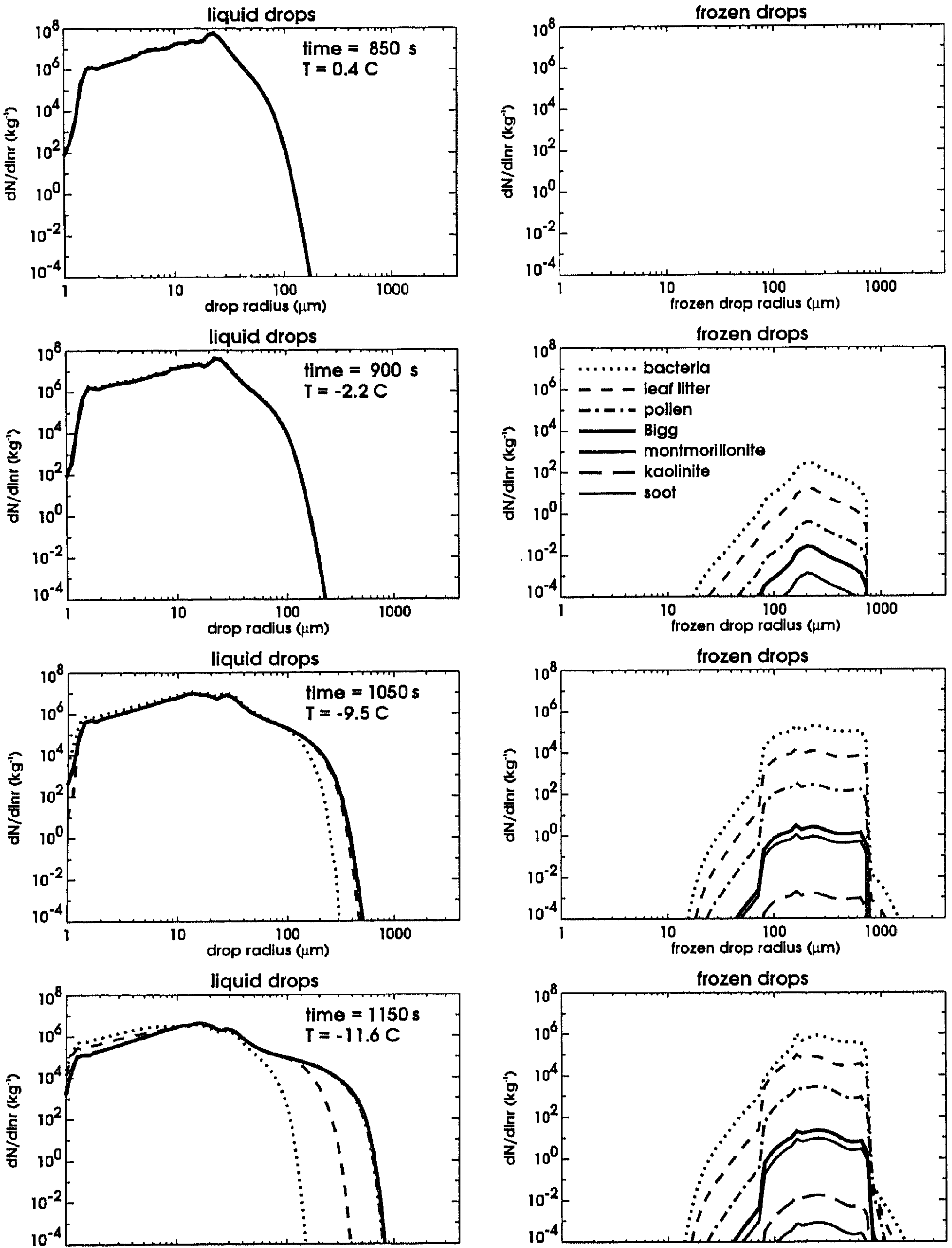

FIG. 3. Number distributions of (left) liquid and (right) frozen drops for model times of 850, 900, 1050, and 1150 s with corresponding temperatures of 0.4°, −2.2°, −9.5°, and −11.6°C, top to bottom, respectively. Line styles for different insoluble particles as described on the second right panel from the top.

The number size distributions of liquid (left) and frozen (right) drops are given for model times of 850, 900, 1050, and 1150 s, and for corresponding temperatures of 0.4°, −2.2°, −9.5°, and −11.6°C, respectively. The times and temperatures were selected shortly before first ice formation set in (850 s) and at ice initiation due to different insoluble particles (900, 1050, and 1150 s). In the model simulations, aerosol particles were activated to drops which grew by water vapor diffusion, collision and coalescence. The drops froze dependent on the temperature, their sizes, and the effects of the insoluble particles. The frozen drops grew further by water vapor diffusion and by riming. As expected, at a positive temperature of 0.4°C, no drops were frozen. At a temperature of −2.2°C, drop freezing set in with the biological particles as the precursors. Drop freezing according to Bigg fits well into the results obtained for montmorillonite particles. No significant effects of the different ice forming nuclei on the liquid drop size distribution appeared at this temperature, because the number of frozen drops was still quite low. The picture changes at −9.5°C. Owing to the good ice nucleating ability of bacteria, there remained significantly fewer liquid drops than in the cases of the other insoluble particles. With regard to the frozen drops, the biological particles were still in greater abundance. Bigg's particles and montmorillonite led to almost identical results, whereas drop freezing owing to kaolinite just becomes initiated. At −11.6°C, drop freezing owing to soot also sets in. Furthermore, one can see that owing to their good ice nucleating abilities, pollen as well as leaf litter significantly affected the liquid drop size distributions, whereas for all other cases the liquid drop size distributions remained almost identical.

These results indicate that the Bigg equation describes drop freezing in the immersion mode well for a "mean" particle, however, a non vigorous treatment of drop freezing is possible with the freezing equations presented in this paper. According to the fractions of the different insoluble particles to the total aerosol particles, the drop freezing in the immersion mode could be clearly described for defined aerosol particle distributions. Soluble particles did not affect the freezing process in the present study as only rather large drops could freeze. As mentioned in section 4b, in these cases the salt concentration in the drops would be too low to cause a significant freezing point depression.

5. Summary and conclusions

In the present study, a method was suggested to consider the influence of both soluble and insoluble aerosol particles on drop freezing in the immersion mode. As most atmospheric aerosol particles contain soluble and insoluble materials, a more realistic treatment of drop freezing would be possible in this way. The higher the content of soluble material the higher is the efficiency of the aerosol particle to act as condensation nucleus. So, drops are formed at aerosol particles, but as long as they are rather small, the freezing point depression owing to the content of soluble material prevents them from freezing. Therefore, they have to grow to larger drops until their salt concentration will be sufficiently low to allow them to freeze. Owing to the content of insoluble particles inside the drops (previously by nucleation and/or later by impaction scavenging), the freezing of rather small drops at rather high temperatures is possible, that means at earlier stages of cloud development and at lower altitudes in the atmosphere.

Based on laboratory experiments two effects were incorporated into the present model calculations: the volume dependence of the freezing temperature and the significant differences of the freezing temperature due to various groups of ice nuclei, that is, soot particles, mineral particles, and biological particles. Most earlier model studies as, for example, Young (1974) and Vali (1994), used nucleation rates related to water samples containing an unknown distribution of different ice nuclei, or, used the Bigg (1953) equation that describes the freezing characteristic of a mean aerosol particle. Incorporating the present model into tropospheric cloud models allows for the application of different ice nucleus distributions with regard to composition, and, therefore, the determination of their special effects on drop freezing. Equation (12), which describes the freezing rate as a function of drop volume and temperature, can be applied to various types of cloud models. Following the above-described model simulation with an air parcel model with sectional microphysics, it is planned to incorporate the presented freezing approach into parameterized models, as well as into more complex models, such as the air parcel model of Bott (1999) and the two-dimensional collision model of Reisin and Wurzler (2001).

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