Using Classical Nucleation Theory for parameterizing immersion freezing in mixed-phase clouds in global climate models

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Using Classical Nucleation Theory for parameterizing immersion freezing in mixed-phase clouds in global climate models

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Abstract

The influence of clouds on the global climate is one of the largest uncertainties in climate models. The optical thickness and the lifetime of clouds, which is influenced by the formation of precipitation, determine if clouds have a warming or cooling impact on the climate. Amongst others these cloud properties are influenced by the formation of ice crystals in the cloud. Ice crystals change the optical thickness of the cloud and can facilitate precipitation formation. They form homogeneously (freezing of solution cloud droplets) or heterogeneously on an insoluble aerosol particle, e.g. mineral dust. Cirrus are formed by both mechanisms, mixed-phase clouds only form by heterogeneous freezing/ice nucleation. Due to the small scale of these processes compared to the resolution of climate models they have to be parameterized in models. The type of ice nucleation parameterization in clouds influences the simulated cloud properties, which have an impact on the radiation budget. In order to reduce the uncertainties of climate models, the ice formation process has to be captured correctly in climate models. This thesis elaborates on different descriptions of heterogeneous ice nucleation in mixed-phase clouds with a focus on immersion freezing.

There are different possibilities how to parameterize immersion freezing. One possibility is a theory based parameterization approach using Classical Nucleation Theory (CNT) in combination with laboratory data. This approach is as physical as possible and covers a wide range of atmospheric conditions. Here a parameterization scheme is evolved based on this approach and subsequently tested against other parameterization schemes in the climate model ECHAM6-HAM2.

The evaluation of uncertainties of CNT is important when using this theory. Due to unconstrained thermodynamic and kinetic parameters, we investigate the sensitivity of the calculated nucleation rate on the different formulations of the unconstrained parameters. Homogeneous freezing data is used to minimize the uncertainty of the theory. Different approaches to describe immersion freezing are afterwards developed by using laboratory measurements of different mineral dust types. The different approaches are evaluated for their microphysical plausibility and the reproducibility of the temperature, size and time dependence of experimental freezing curves. The best approaches are implemented into ECHAM6-HAM2. Technical details and arising issues when implementing the schemes are also discussed.

The newly developed CNT parameterization scheme is tested in the context of an Arctic case study (M-PACE). It is compared to different parameterization schemes. The simulations show that the ice water content of a cloud changes with the use of different parameterization schemes.
Additionally it is investigated how sensitive the results with the new CNT scheme are to the used mineral dust type. Depending on the mineral dust type more or less ice is formed inside the cloud.
Zusammenfassung


implementiert. Technische Details und Schwierigkeiten, die bei der Implementierung auftauchen können, werden ebenfalls erörtert.

Abstract

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Introduction

The following chapter motivates the thesis, explains the climate impact of clouds & aerosols and illustrates how freezing takes place in clouds and how aerosol particles can act as key players for the freezing processes. An outline in the end gives an overview which topics are discussed within this thesis.
Motivation

Clouds play an important role in the Earth’s climate system due to their strong impact on the energy balance (Chahine, 1992, Solomon et al., 2007). They transport heat and moisture in the atmosphere (hydrological cycle) (Quante, 2004). The distribution of moisture and cloudiness influences precipitation (rain and snow). The dynamical features of clouds (updrafts) carry energy, moisture and momentum, trace gases and aerosol particles from the surface to the upper troposphere (Boucher et al., 2013). Additionally, a lot of chemical reactions take place in clouds. Microphysical processes in clouds such as the formation of the cloud itself, phase changes and the formation of precipitation, are strongly influenced by aerosol particles.

Due to their small spatial extent and the complexity of cloud microphysics and precipitation formation, their interactions with aerosol particles have to be parameterized in general circulation models (GCMs). GCMs are based on physical principles to represent the climate system and to perform climate predictions, e.g., for the IPCC scenarios. In the recent years parameterization schemes for cloud and aerosol processes and interactions have been improved significantly, but they remain the largest uncertainty in GCMs (Boucher et al., 2013). This uncertainty also leads to uncertainties in cloud feedbacks on the climate system and is a major reason for the differences in the climate response by different GCMs for a doubling of CO\textsubscript{2} (Dufresne and Bony, 2008). To understand the changes in the climate system it is therefore essential to improve the representation of cloud and aerosol processes (Arakawa, 1975, 2004; Bony et al., 2006; Cess et al., 1989).

One issue why a complete representation of microphysical processes in clouds is challenging is the lack of knowledge concerning some of these processes (Boucher et al., 2013). Especially in ice and mixed-phase clouds, which are clouds containing water and ice particles, aerosol-cloud interactions are rather complex compared to pure liquid clouds, because of the variety of mechanisms taking place in these clouds. One of the unknown key players is atmospheric ice formation. E.g., Hoose et al. (2010), Fowler and Randall (1996), Storelvmo et al. (2011), DeMott et al. (2010), Lohmann (2002) and Lohmann and Hoose (2009) show that climate model simulations change significantly if different parameterization schemes are used for atmospheric ice formation. Thus it is important to understand and improve parameterizations for atmospheric ice formation.

The following thesis focuses on freezing processes in mixed-phase clouds. For that purpose a new parameterization of the most dominant freezing process in mixed-phase clouds - immersion freezing - is developed based on a theoretical approach and laboratory measurements and implemented into the ECHAM6-HAM2 GCM (Siewers et al., 2013). In the following the basic physical principles of the role of clouds in the climate system, aerosol cloud interactions and
1.1 The role of clouds in the Earth’s radiation budget

The energy of the Earth-atmosphere system is determined by the incoming and outgoing radiation to space (Peixoto and Oort [1992]). Clouds absorb and scatter shortwave radiation (solar radiation) and absorb and re-emit longwave radiation (terrestrial radiation) the amount of which depend on their physical properties (see Fig. 1.1). The scattering of shortwave radiation leads to a cooling of the climate system and is called the albedo effect of clouds (Solomon et al. [2007]). On the contrary re-emission of longwave radiation back to the surface causes a warming (trapping of radiation) and is called greenhouse effect of clouds. Clouds and their radiative effects are one of the major influences on the radiative fluxes in the atmosphere (Boucher et al. [2013]).

Physical properties which determine the net radiative effect of clouds are the temperature, vertical extent and optical thickness (water content, composition, etc.) of the cloud, its location and its temporal evolution (Zhang et al. [1999]). Different cloud types have contrasting radiative effects. High cool clouds (cirrus) are optically thin clouds because the water vapor is quite sparse at the altitudes/temperature they are forming. Another factor is that they consist of ice crystals only. Due to their low temperature compared to the surface they emit less longwave to space than a cloud free atmosphere would and thus cause a warming of the climate. Low warm clouds are optically thick. They cause a net cooling due to scattering of the incoming solar ra-
diation (increase in planetary albedo) when they occur over a dark surface (ocean, vegetation) [Fueglistaler and Fu (2006)]. Their greenhouse effect is negligible, because their temperature is similar to the surface temperature. Mid-level clouds like mixed-phase clouds have a net cooling effect, which is less pronounced compared to low warm clouds due to their height and lower optical thickness.

One physical parameter which influences the optical thickness of clouds (especially for mixed-phase clouds) and thus their radiative properties is the microphysical composition of clouds including size, number concentration and phase of cloud particles. A smaller number of cloud particles leads to a lower optical thickness (for the same total liquid water content), so that the cloud reflects less sunlight, which causes a positive radiative forcing as compared to a cloud with a large number of cloud particles (Choi et al., 2010). In the case of mixed-phase clouds that means that these clouds are very sensitive to the number of ice crystals formed by heterogeneous freezing (DeMott et al., 2010).

1.2 The role of aerosol particles in the Earth’s radiation budget

Aerosol particles have various impacts on the Earth’s radiation budget and the climate. They can interact with radiation directly by absorbing and scattering radiation. On the other hand they have a strong influence on clouds, which indirectly influences the climate and weather (Houghton et al., 2001). The indirect effects refer to aerosol induced changes in radiative properties, amount and lifetime of clouds by microphysical processes and precipitation [see simplified sketch in Fig. 1.2; Yin et al. (2002)]. Hence the cloud albedo and the Earth’s radiation budget (radiative forcing) is changed.

Figure 1.2: Sketch showing the influence of aerosol particles on clouds and climate.
Aerosols and clouds interact with each other. Whereas aerosol processing in (and below) clouds change the total amount and characteristics of the aerosol population, the aerosols itself influence the microphysical properties of clouds. How the cloud properties are affected by aerosol particles depends on the cloud type, mechanism of interaction and on the aerosol itself (Costa et al., 2004). Aerosol-cloud interactions can lead to a cooling or warming within the climate system. The net effect is estimated to be negative for the industrial era (Boucher et al., 2013).

Aerosol particles can act as cloud condensation nuclei (CCN) or ice nuclei (IN) facilitating nucleation processes. CCN are essential for the formation of low warm clouds. When more CCN are available the cloud would form more cloud droplets. Assuming a constant liquid water content (LWC) within the cloud that would lead to more and smaller droplets. Since a higher population of smaller droplets results in a higher total surface area of the droplets the cloud scatters more solar short wave radiation back to space. The cloud albedo is enhanced in this case (Twomey-effect or cloud-albedo effect) leading to a cooling. This effect can partly compensate the warming by CO₂ (Solomon et al., 2007).

In cold clouds the impact of aerosol particles is less understood. Aerosol particles acting as IN are essential for the phase change in mixed-phase clouds and have an influence on cirrus clouds as well. Both cloud types can be very sensitive to the aerosol species and concentration. E.g. an increase in IN in mixed-phase clouds can lead to a glaciation of the cloud [glaciation indirect effect; DeMott et al. (2010), Lohmann (2002)]. Choi et al. (2010) showed that dust occurrence and supercooled liquid water content are negatively correlated in mixed-phase clouds. A glaciated cloud precipitates faster and therefore has a decreased lifetime [cloud-lifetime effect; Haywood and Boucher (2000), Rogers and Yau (1989)]. That yields in a decrease of the cooling effect of this mixed-phase cloud [decrease in optical thickness and lifetime; Lohmann and Feichter (2005)].

Other indirect aerosol effects (adjustments) are the riming indirect effect (fewer CCN lead to bigger cloud droplets and therefore more riming and an enhanced ice crystal mass) and the thermodynamic indirect effect (fewer CCN and thus bigger cloud droplets could also lead to more secondary ice production and therefore an enhanced ice crystal number).

At the current state of research it is not possible to predict the concrete influence of IN on the climate (DeMott et al., 2010). With limited knowledge about the influence of aerosol particles on clouds and the influence of cloud-aerosol processing on aerosols does the net radiative effect on the radiation budget remain uncertain. Besides potential feedback processes are not understood yet. Thus it is important to improve understanding of the interaction of aerosols with ice and mixed-phase clouds.
1 Introduction

1.3 Atmospheric ice formation

Atmospheric ice formation has an impact on a broad range of climate relevant processes: the radiative properties of clouds (see section 1.1), precipitation, cloud dynamics, chemical processes (Geiger et al., 2001) and lightning (Sherwood et al., 2006). More than 50% of the global precipitation is initiated via the ice phase (Lau and Wu, 2003). Especially in mid latitudes IN and their interaction with mixed-phase clouds are an essential component of the precipitation cycle (DeMott et al., 2010, Lohmann, 2002, Zeng et al., 2009). The latent heat release from the phase change when forming ice, warms the environment and influences the dynamics inside the cloud. The buoyancy is increased and thus the vertical cloud development also increases. Therefore ice formation can influence the vertical extent of mixed-phase clouds (Baker, 1997). The change in vertical extent can additionally influence precipitation formation (Zubler et al., 2011).

The mechanisms of atmospheric ice formation are very important to understand the climate impact of clouds and reduce the uncertainty in climate model projections.

The formation of ice crystals and ice clouds is a function of temperature $T$, water saturation/supersaturation, the presence of IN and the age of the cloud (time). There are typically two cloud types containing ice crystals: mixed-phase clouds and cirrus clouds. While mixed-phase clouds contain water droplets and ice crystals at the same time, cirrus clouds are pure ice clouds. Approximately 20% of the global cloud coverage are mixed-phase clouds, 40% are cirrus clouds (estimations based on zonal means simulated by ECHAM6-HAM2; the spread of the (literature) values are quite large, e.g. 16.7% global cirrus coverage (Sassen et al., 2008) compared to 34% global cirrus coverage (Warren et al., 2007)). The conditions for the formation of ice crystals are significantly different in both cloud types.

Cirrus clouds are high-level clouds (mean cloud base is 6 km or higher (Lynch et al., 2001)). Due to the high altitude the temperature and humidity is low. The latter limits the crystal growth. Therefore ice crystals in cirrus clouds are often smaller than 100 $\mu$m and low in number with typical ice crystal concentrations between 0.001 and 10 particles cm$^{-3}$ (Krämer et al., 2009). Hence cirrus clouds are optically thin clouds.

Mixed-phase clouds form at warmer temperatures at water saturated conditions. At coexistence of ice crystals and supercooled cloud droplets, the crystals grow rapidly due to the Wegener-Bergeron-Findeisen process. The Wegener-Bergeron-Findeisen process explains this growth by the difference in saturation vapor pressure. The saturation vapor pressure over ice is smaller than the one over water. That leads to a diffusion gradient. The supercooled cloud droplets evaporate and the water vapor resublimates at the ice crystals leading to a growth of the ice crystals in the expense of the supercooled cloud droplets. The process is most efficient at 261.15 K because the difference of the saturation vapor pressure is the largest at this temperature. The Bergeron-Findeisen process favors the precipitation formation.
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Due to the conditions in the cloud ice formation can take place homogeneously or heterogeneously, which is explained in more detail in the following.

**Homogeneous freezing**

Homogeneous freezing of a supercooled droplet happens due to spontaneous temperature and density fluctuations inside the droplet \(\text{Pruppacher and Klett, 2000}\). These fluctuations lead to the nucleation of small ice embryos, which initiate fast crystallization of the whole droplet after a certain size threshold of one ice embryo is reached \(\text{Haag et al., 2003}\). The ice embryo reaching this critical size is called ice germ. The statistical probability of an ice germ in the droplet is a function of temperature, water saturation and drop size. The smaller the droplet, accordingly the water volume, the fewer water molecules are available for the formation of ice embryos. The onset temperature at which homogeneous freezing potentially takes place is lower in this case, e.g. a 1 µm droplet freezes at 233.15 K, whereas a 100 µm droplet can already freeze at 238.15 K \(\text{Wallace and Hobbs, 2006}\). The conditions for homogeneous freezing can only be reached in cirrus clouds and anvils of deep convective clouds (anvil cirrus). For typical cirrus clouds an onset temperature for homogeneous freezing is usually around 235.15 K, e.g. as defined in ECHAM6-HAM2. Besides the cloud has to be at water saturation with respect to water or in the case of the freezing of solution droplets at saturation with respect to the solution. Because of that homogeneous freezing highly depends on the cloud updraft velocities, which determine the supersaturation with respect to ice.

Note that in principle also a phase transition from the vapor phase directly to the ice phase is possible, but as the water saturation has to be higher for this transition it is unlikely to happen in the Earth’s atmosphere.

**Heterogeneous freezing - one pathway of aerosol cloud interactions**

The formation of ice crystals can also occur via heterogeneous freezing, where the phase transition takes place on aerosol particles. These aerosol particles, called IN, lower the energy barrier for the phase change. The surface properties of the solid aerosol particle involved in the process influence the onset temperature of the phase transition. The required onset temperature is higher and the critical supersaturation lower as compared to homogeneous freezing, but aerosol particles are needed which can act as IN. More information about the physical principle of heterogeneous freezing can be found in chapter 4.

The term heterogeneous freezing is a collective term for different freezing/nucleation mechanisms. There are four different heterogeneous freezing modes (pathways), which result in ice crystals \(\text{Vali, 1985a}\):
• **Immersion freezing:** The IN is immersed in a cloud droplet (may have acted as CCN). The cloud droplet freezes as soon as the onset temperature for the phase change is reached.

• **Condensation freezing:** Water vapor is condensating on the IN (at water saturated conditions) forming temporarily a supercooled cloud droplet, which freezes immediately. The IN is an effective CCN as well in this case. Note that this pathway is experimentally difficult to distinguish from immersion freezing. Therefore immersion freezing is often used as a surrogate for condensation and immersion freezing.

• **Contact freezing:** A supercooled droplet is colliding with an IN and freezes instantaneously. The collision is initiated by phoretic processes, Brownian motion or inertia of the particles. This mechanism is limited by the collision efficiency. A special case for this mechanism is contact freezing inside-out, where the IN is moving from the inside to the outside of the droplet initiating the freezing when colliding with the outer surface (Durant and Shaw, 2005).

• **Deposition nucleation:** Water vapor deposits on the IN. This phase transition can happen below water saturation as soon as saturation with respect to ice is exceeded.

All of these pathways are shown in Fig. 1.3.

![Freezing modes](http://example.com/freezing_modes.png)

Figure 1.3: Freezing modes. Modified from Hoose and Möhler (2012).

Mixed-phase clouds are too warm for homogeneous freezing to happen and therefore (mostly) based on the mechanism of heterogeneous freezing. Lidar observations show that ice crystals
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form from liquid droplets. This is an indication that deposition freezing is playing a minor role in mixed-phase clouds (Ansmann et al., 2008). Modeling studies, e.g. Hoose et al. (2010) confirm that immersion freezing is found to be the dominant process.

Contact freezing seems to be negligible for both mixed-phase and cirrus clouds despite laboratory studies show that contact nucleation is the most efficient mechanism, because freezing temperatures are the highest (Ladino et al., 2011, Lüönd et al., 2010). The reason is the limitation due to low collision rates and/or the small presence of aerosol particles, which are not yet immersed in droplets.

In cirrus clouds deposition freezing and immersion freezing of solution droplets is relevant alongside homogeneous freezing.

1.3.1 Characteristics of ice nuclei

Ice Nuclei (IN) are aerosol particles which are able to initiate either the freezing process of (supercooled) cloud droplets or ice nucleation from the vapor phase (acting as a deposition site for water vapor). They enable the formation of ice particles in a cloud at relatively high temperatures and therefore are critical for the existence of ice in clouds (DeMott et al., 2010). Freezing of pure cloud droplets without the help of IN only happens in cirrus clouds, in most cases the temperatures are too high for freezing of pure cloud droplets.

Only a small percentage of the total number of aerosols is able to act as an IN (free troposphere 0.01 particles cm$^{-3}$; in dust layers up to 1 particles cm$^{-3}$) [DeMott et al. (2003a,b)]. 0.01 particles cm$^{-3}$ in the free troposphere relates to only 0.001% of the CCN in the atmosphere. Whether a particle can potentially (in case the meteorological conditions are suitable) act as an IN or not depends on the composition and characteristics of the particle. However, the exact mechanisms are not completely understood yet.

At field measurements different attempts have been made to investigate the composition of atmospheric IN, e.g. Kamphus et al. (2010) and the IN activity of different substances, e.g. DeMott et al. (2003a,b), Kamphus et al. (2010), Petters et al. (2009), Phillips et al. (2008), Pratt et al. (2009). The main aerosol particles acting as an IN are listed in the following (Hoose and Möhler, 2012, Vali, 1985a) and shown in Fig. 1.4.

- **Mineral dust**: Mineral dust particles, especially from the Sahara, are effective IN, also in great distances from the source regions (DeMott et al., 2003b) [Sassen et al. (2003)]. Mineral dust seems to be the dominant IN, which has been confirmed by many measurements, e.g. Chou et al. (2011), DeMott et al. (2003b), Kamphus et al. (2010), Klein et al. (2010), Sassen et al. (2003). While mineral dust particles are transported through the atmosphere the composition and characteristics of the mineral dust particles changes (due to chemical
...and physical (coagulation) processes. The IN ability of dust depends therefore on the origin of the airmass.

- **Black Carbon (BC) and Biomass burning particles**: Whether BC is a good IN is still an open question. There are studies, e.g. Petters et al. (2009) that suggest a local influence of black carbon on the IN concentrations at biomass burning events in South America. That could explain the low liquid water content in South American clouds. Conflicting evidence is presented in Prenni et al. (2009). They show that the IN activity of soot from biomass burning activity is very low.

- **(Primary) Bioaerosols**: Bioaerosols such as pollen, bacteria, fungal spores etc. can act as IN, for instance in the Amazon bassin or in wave clouds over North America (Pratt et al., 2009, Prenni et al., 2009).

- **Volcanic ash**: The importance of volcanic ash as an IN is highly unknown. However, volcanic ash clouds have different characteristics compared to meteorological clouds. The number of IN in volcanic clouds is higher, such that they can be over seeded (hindering the Bergeron-Findeisen process). An experimental study show that volcanic ash from the Eyjafjallajökul eruption in 2010 has good IN activity (Hoyle et al., 2011).

- **Other species**: Other ice active components are metallic particles (DeMott et al. 2003a), metal oxides (Worringen et al. 2015), potassium, sulfate, carbon (Kamphus et al., 2010) or carbonaceous material (Worringen et al. 2015) and organic particles (Kamphus et al. 2010). The role of organic, organic semi-solid and glassy organic aerosol particles is unclear (Hoose and Möhler 2012, Murray et al. 2012). Sea-salt particles seem not to be ice active (DeMott et al. 2010). Different studies yield that salts like NaCl, NH₄Cl, NH₄NO₃, (NH₄)₂SO₄ and CaCl₂ are not ice active above 255.15 K (Pruppacher and Klett 2000).

To overcome uncertainties concerning the ice nucleating ability different species are investigated by laboratory studies (Hoose and Möhler 2012, Murray et al. 2012). Although it is not yet investigated in detail which characteristics make a good IN, there are some characteristics which seem to result in good ice nucleating abilities:

- **Insolubility**

- Comparable or larger size than that of the ice germ: The larger the particle, the larger is the the surface area, which facilitates the phase transition. In the case of Arizona test dust (ATD) a size larger than 100 nm increases the probability of having one active site (area on the IN where ice nucleation is initiated) which facilitated the phase change (Marcolli et al. 2007).
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- Crystallography: If the particle has an atomic arrangement which is very similar to ice (lattice match) and if the molecular distances are also similar it is very likely that this particle acts as an IN, e.g. kaolinite particles, Agl (Evans, 1965).

- Free hydrogen bonds on surface, e.g. in the case of organics.

- Cracks, impurities and cavities on the surface of the aerosol particle.

Interaction with gases (SO₂, NH₃, NO₂) and small particles (organics, sulfates) may change the characteristics of the aerosol particles and hence might affect the ability to act as an IN (Prenni et al., 2009; Sullivan et al., 2010a). A reason could be the modification of the IN surface. Especially sulfuric acid changes the IN surface irreversible (Sullivan et al., 2010b).
Figure 1 A: Different aerosol particles and their sources: mineral dust (A,B), soot (C,D), volcanic ash (E,F) and pollen (G,H) [A,E,G,H: Wikimedia Commons; B: Université Libre de Bruxelles; C: Flickr; D: NASA, Univ. of Denver; F: U.S. Geological Survey].
1.4 Outline of the thesis

Parameterization schemes for immersion freezing are essential for the representation of mixed-phase clouds in GCMs and therefore might influence the outcome of climate simulations. The objectives of this thesis are to gain insight into:

1. The existing possibilities to parameterize immersion freezing in GCMs
2. CNT and its sensitivity to kinetic and thermodynamic parameters in the case of homogeneous and heterogeneous freezing
3. How immersion freezing measurements can be used to develop a CNT based parameterization scheme
4. Which technical issues can arise when implementing a CNT based scheme into a GCM
5. How different parameterization schemes compare to each other (in the framework of the Arctic case study M-PACE)

The overall aim is to develop an approach how to use a Classical Nucleation Theory (CNT) based theoretical approach for immersion freezing in the ECHAM6-HAM2 GCM.

Different possibilities of parameterization schemes for immersion freezing in GCMs are explained in chapter 2 (objective 1). For each type of a parameterization scheme one example is explained in more detail. The advantages and disadvantages of certain schemes are worked out and summarized. This motivates the aim of the thesis and puts it into a broader context.

The concept of CNT is elaborated in chapter 3 with the focus on homogeneous freezing. Because CNT contains some unconstrained thermodynamic and kinetic parameters, it is analyzed how sensitive the theory is to these parameters and which uncertainties and consequences arise due to this (objective 2). Homogeneous freezing measurements are used to constrain thermodynamic and kinetic parameters of the freezing process.

The extension of CNT in the case of immersion freezing is introduced in chapter 4. Additional information about the microphysical properties of certain IN -the contact angle- is needed to describe the freezing process. Therefore laboratory data of the immersion freezing ability of different mineral dust particles (kaolinite, illite, montmorillonite, ATD and microcline) is used to estimate the parameters describing the influence of the IN on the freezing process. These can be incorporated into the parameterization scheme (objective 3). Different approaches to describe the influence of the IN on the freezing process are compared and evaluated by the use of three criteria. They are the microphysical validity of the parameters (partly emerging from
Chapter 3) and the reproducibility of dependence on temperature, as well as on particle size and time of the freezing process. At the end of this chapter two CNT schemes are recommended for the use in ECHAM6-HAM2.

The ECHAM6-HAM2 GCM is introduced in Chapter 5 highlighting the representation of aerosols and mixed-phase clouds in the model and explaining the new CNT based parameterization schemes in detail in the context of ECHAM6-HAM2 and the technical implementation. In this chapter the difficulties arising for the implementation of CNT based parameterization schemes is also treated (objective 2).

Different parameterization schemes including the newly evolved CNT based schemes are tested and compared in Chapter 6 in the context of the M-PACE case study (objective 3) using the single column model setup of ECHAM6-HAM2, which is explained in Chapter 5. The M-PACE case study is focused on microphysical processes in Arctic mixed-phase clouds, thus providing an interesting test platform for immersion freezing parameterization schemes.

Chapter 7 summarizes the major findings of this thesis and gives some ideas what could be further investigated and additionally implemented or adapted in ECHAM6-HAM2.
Freezing parameterization schemes for immersion freezing in GCMs

Immersion freezing in mixed-phase can be parameterized to describe this unresolved process in GCMs using different methodical approaches. Four methods to gain parameterization schemes are introduced including advantages and disadvantages. Additionally four parameterization schemes, which are used later on in this thesis, are presented.
Introduction

Heterogeneous freezing can be parameterized following one of the four methods:

1. Based on field-measurements.

Some field measurements in mixed-phase clouds were done in the last years, mostly on airplanes. The data gained from a flight through a mixed-phase cloud gives some indication what happens in the atmosphere. This is then used to develop an empirical parameterization scheme which describes the freezing process. Generally, the number concentration of ice particles is described as a function of temperature $T$ and/or supersaturation with respect to ice $S_i$. Freezing is described as an instantaneous process, meaning that once certain $T/S_i$ conditions are reached droplets freeze immediately - no time dependence of freezing is taken into account. Parameterization schemes which assume singular freezing behavior are called deterministic schemes.

The main advantage of field based parameterization schemes is that the process is investigated under real atmospheric conditions. Doing measurements at real conditions is at the same time the main caveat of this method because the measurement conditions cannot be fully controlled (depending on the instrumental setup). Moreover measurements can also not be repeated for the same conditions. The resulting scheme is always limited to the case of the measurement. Therefore developed parameterization schemes can be very different and specific for the region where the campaign took place.

The approach of DeMott et al. (2010, 2015), which is based on measurements with a continuous flow diffusion chamber (CFDC) on different field campaigns, is described in more detail in section 2.1. Other examples are the frequently used scheme of Meyers et al. (1992), the Phillips et al. (2008) scheme, which is an extension of the former and the Tobo et al. (2013) scheme, which is using the same principle as DeMott et al. (2010).

2. Based on laboratory-measurements.

Heterogeneous freezing can be studied in various setups in the laboratory. Often frozen fractions of a number population of droplets or freezing onset temperatures are measured. The data can be used to develop empirical parameterization schemes to describe the investigated freezing process. Freezing is described as a function of experimental conditions: temperature $T$, supersaturation $S_i$ and time $t$. The latter is not a variable/determining factor of the empirical function in all cases. Sometimes, e.g. in Lohmann and Diehl (2006), the process is described as a function of a cooling rate instead of $T$ and $t$ separately. The main advantage of laboratory based parameterization schemes is that conditions, during which the freezing process takes place, can be controlled in the experiment. The main caveat of this method is the limitation to experimental conditions. For the use in global models the
results are often extrapolated without knowing if that is reasonable. Another caveat is the spread of measurement results, e.g. the freezing onset temperature of dust particles for different experimental setups (cold stage experiments, cloud chamber experiments, etc.). The reason is (in addition to instrumental uncertainties) that determining factors are different, e.g. measurements can be related to the droplet volume (Diehl and Wurzler, 2004) or to the aerosol surface area (Murray et al., 2011). Two example approaches are explained in more detail in section 2.2: the Lohmann and Diehl (2006) parameterization scheme based on wind-tunnel studies and the Niemand et al. (2012) parameterization scheme based on measurements in a cloud chamber. Other examples for a laboratory based approach are Murray et al. (2011), Atkinson et al. (2013), Connolly et al. (2009), Niedermeier et al. (2010), Welti et al. (2012).

Based on theory.

Another approach is to describe the freezing process based on a theory or a theoretical framework. For freezing this is not trivial because water, especially supercooled water, is a complex system with many unknowns. Classical Nucleation Theory (CNT) is one theoretical framework describing the freezing process stochastically as a function of $t$, $T$ and $S_i$. It is assumed that freezing is a continuous process [as shown in some laboratory experiments (Murray et al., 2012; Welti et al., 2012)]. Stochasticity of the freezing process means that with increasing time more droplets freeze. The difference compared to singular (deterministic) schemes is that this time-dependence is taken into account. However, $T$ is the most important factor to trigger the freezing process (Ervens and Feingold, 2013; Welti et al., 2012).

CNT is used as a parameterization scheme in GCMs or parcel models, e.g. Khvorostyanov and Curry (2004), Khvorostyanov and Curry (2005), Khvorostyanov and Curry (2000), Liu et al. (2007), Eidhammer et al. (2009), Barahona and Nenes (2009), Hoose et al. (2010), Storelamo et al. (2011), Ervens and Feingold (2012), Morales Betancourt et al. (2012), Wang et al. (2014). The main advantage is that a theoretical scheme is valid over the whole temperature and supersaturation range and does not have any limitations in the $T$-$S_i$-space coverage. The main caveat is the missing “reality” proof of the theory, especially in the temperature and supersaturation conditions which cannot be investigated in the laboratory. The theory itself can introduce uncertainty due to missing constraints because of the lack of knowledge about the microphysics of water. To constrain CNT input from laboratory measurements might be used, reducing the coverage of the $T$-$S_i$-space.

Based on small-scale models.
Small-scale models, e.g. large eddy simulations (LES) are capable to capture the freezing process explicitly and therefore enhance the understanding of the process itself. Starting from a sophisticated approach, easier frameworks might be developed for the use in GCMs. Heterogeneous freezing schemes have been tested e.g. in the parcel model ACPIM (Aerosol Cloud Precipitation Interaction Model) [Connolly et al. (2009)], in COSMO LES (Paukert and Hoose 2014a) and in MIMICA (Savre and Ekman 2015).

Each method has different advantages and disadvantages. The following Table 2.1 summarizes the characteristics of the different parameterization schemes emerging from different methods. The most important criteria for a suitable parameterization scheme to describe mixed-phase clouds in a GCM is the coverage of the $T$-$S_i$-space in the relevant range for mixed-phase clouds. That is close to $S_i = 1$ and in a temperature range between the melting point and the homogeneous freezing temperature (approximately 238 K). This criterion is difficult to fulfill for most empirical schemes as they are only estimated under certain conditions. This might cause problems in a GCM because the parameterization scheme might not hold for future atmospheric conditions or conditions, which are untypical. That was seen e.g. in an Arctic case by Prenni et al. (2007), where the Meyers et al. (1992) scheme did not work due to the different conditions of the Arctic compared to the mid-latitudes, where the scheme was developed. In another study by Mason et al. (2015) it was shown that extrapolating empirical schemes can cause deviation from field measurements in the extrapolated temperature range.

To study aerosol-cloud interactions in different environments another essential criteria is that the parameterization scheme distinguishes between different aerosol species (IN). This is e.g. important for estimates of the anthropogenic aerosol forcing.

An ideal parameterization scheme would be a merged field, laboratory and theory based parameterization.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>1 field</th>
<th>2 laboratory</th>
<th>3 theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freezing behavior</td>
<td>singular</td>
<td>singular/stochastic</td>
<td>stochastic</td>
</tr>
<tr>
<td>Time dependence</td>
<td>✗</td>
<td>✗/✓</td>
<td>(✓)</td>
</tr>
<tr>
<td>Coverage $T$-$S_i$-space</td>
<td>✗</td>
<td>✓</td>
<td>(✓)</td>
</tr>
<tr>
<td>Attribution to aerosol types</td>
<td>✗/(✓)</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Reality check</td>
<td>✓</td>
<td>✗</td>
<td>✗</td>
</tr>
</tbody>
</table>

Table 2.1: Characteristics of the parameterization schemes gained by different methods. Table modified from C. Hoose (personal communications).
2.1 Field based parameterization schemes: the DeMott et al. parameterization

The first parameterization schemes based on field measurements were the schemes of Fletcher (1962), Cooper (1986) and Meyers et al. (1992), which consist of very simple formulations of IN number concentration as a function of \( T \) and \( S_i \). These schemes do not account for the temporal and spatial variability of IN related to changes in the overall aerosol concentration. The IN number concentrations vary over a range of three orders of magnitude at any \( T \), which might be due to differences in aerosol particle types over space and time.

The DeMott et al. (2010) parameterization scheme is a singular scheme based on CFDC measurements of immersion/condensation freezing. It is still a simple parameterization scheme but more sophisticated compared to Fletcher (1962) and Meyers et al. (1992), because freezing is described not only as a function of \( T \) and \( S_i \) but additionally the particle size dependence of freezing is taken into account. The IN number concentration \( n_{\text{IN}} \) [cm\(^{-3}\)] is linked to the total amount of available aerosols above a certain threshold size (aerosol particle diameter). This threshold size is estimated to be 0.5 \( \mu \)m. The size is an indicator for the aerosol surface area. Measurements of IN and total aerosol concentrations (mostly done on air planes at or near cloud level) from nine field studies at different locations over 14 years were taken to derive the parameterization. Freezing is described as a power law function of \( T \):

\[
    n_{\text{IN}} = a \cdot (273.16 K - T)^b \cdot (n_{\text{aer},0.5})^{(c \cdot (273.16 K - T) + d)}, \tag{2.1}
\]

with \( n_{\text{aer},0.5} \) the aerosol number concentration of aerosols larger than 0.5 \( \mu \)m [std. cm\(^{-3}\)], \( a = 5.94 \cdot 10^{-8} \), \( b=3.33 \), \( c=0.0264 \) and \( d=0.0033 \).

The specific composition of the aerosol particles is not taken into account, what makes the scheme a simplified version of the Phillips et al. (2008) parameterization scheme.

In 2015 the scheme was updated and specified for mineral dust (adding an exponential term to the formula) to:

\[
    n_{\text{IN}} = c f \cdot 10^{-3} \cdot (n_{\text{aer},0.5})^{(\alpha \cdot (273.16 K - T) + \beta)} \cdot \exp(\gamma \cdot (273.16 K - T) + \delta), \tag{2.2}
\]

with the instrument correction factor \( c f \), the parameters \( \alpha, \beta, \gamma \) and \( \delta \), which have to be estimated by the measurement data (aerosol specific if possible). The parameters were estimated for mineral dust by using a combination of field and laboratory measurements yielding: \( c f = 1 \), \( \alpha = 0 \), \( \beta = 1.25 \), \( \gamma = 0.46 \) and \( \delta = -11.6 \).
2 Freezing parameterization schemes for immersion freezing in GCMs

2.2 Laboratory based parameterization schemes: the Lohmann-Diehl and the Niemand et al. parameterization

The Lohmann-Diehl parameterization scheme

In the scheme of Lohmann and Diehl (2006) immersion (and contact) freezing is based on empirical relations obtained from wind tunnel studies summarized in Diehl and Wurzler (2004). The freezing process is characterized by an exponential rate function (analogous to CNT, but simplified) of $T$ and a cooling rate. The freezing temperature is assumed to be independent of the size of the particles. The chemical composition of the IN is taken into account. The empirical relation is derived for two mineral dust types (kaolinite and montmorillonite) and black carbon (BC).

The scheme is used in the standard setup of ECHAM6-HAM2. The freezing rate is expressed as follows:

$$J_{imm}[m^{-3}s^{-1}] = a \cdot N_{a,imm} \exp(a \cdot (273.15 K - T)) \cdot \frac{dT}{dt} \cdot \frac{\rho_{air} \cdot q_l}{\rho_l}$$

(2.3)

with $N_{a,imm}$ the number of immersion nuclei, $\rho_{air}$ the air density, $\rho_l$ the density of the cloud droplet, $q_l$ the cloud liquid water mass-mixing ratio in the cloud and $a = K^{-1}$. Immersion freezing only takes place if there is a cooling rate, which means $\frac{dT}{dt}$ has to be smaller than zero. The number of immersion nuclei $N_{a,imm}$ is obtained from the fraction of aerosol particles made up by hydrophilic BC and accumulation mode dust aerosols multiplied by a temperature dependence (onset-freezing temperatures) of individual species $x$:

$$N_{a,imm} = \sum_x c_x \frac{N_{imm,x}}{N_{aer,tot}} = N_{a,imm,dust} + N_{a,imm,BC}$$

(2.4)

where $c_x$ is 32.3 for montmorillonite, 6.15$\times10^{-2}$ for kaolinite and 2.91$\times10^{-3}$ for BC. The weighting factors for each aerosol species are derived from the measurements and used as a constant value in the parameterization scheme. It would be more appropriate to calculate the number of immersion nuclei $N_{a,imm}$ interactively in the model.

This scheme is an easy description of the aerosol specific freezing process. However, it requires knowledge about the number of IN which can be difficult to estimate in a GCM. In addition to that it neglects the size-dependence of the IN. Note that the interpretation of the measurement data is difficult because it is not known how many aerosol particles have been immersed in one droplet. That leads to a bad reproducibility of the experiment.
This scheme, described in Niemand et al. (2012) for immersion freezing of natural dust, is a deterministic scheme based on the approach of Connolly et al. (2009). It is derived from measurements carried out at the “Aerosol Interaction and Dynamics in the Atmosphere” (AIDA) cloud chamber at KIT, Karlsruhe. A detailed description of the cloud chamber and the measurements can be found in Niemand et al. (2012).

In this approach it is assumed that ice nucleation is a function of $T$ and particle surface area $A_{IN}$. Ice nucleation occurs on localized sites, called active sites. The concept of active sites has been proposed by Langham and Mason (1958) and is a continuation of the deterministic approach. Active sites are microphysical areas on the particle where water can be captured or adsorbed. These microphysical areas are structural imperfections of the surface such as cracks, steps or contamination by a few molecules. The number of active sites decreases with increasing temperature and depends also on the composition of the aerosol particle. They are assumed to be equally distributed over the dust particle surface area.

In Connolly et al. (2009) the change of the number of ice active aerosol particles (IN) in the size bin $j$, $N_{i,j}$, with respect to $T$ is:

$$\frac{dN_{i,j}}{dT} = (N_{i,j} - N_{tot,j}) \cdot A_{j}, k(T),$$

(2.5)

where $N_{tot,j}$ denotes the total number of aerosol particles in the size bin $j$ and $A_{j}$ for the dust particle surface area in the same size bin. The surface site density of ice active sites $n_{s,IN}$ as a function of $T$ can be determined by integrating the factor $k(T)$ over the whole temperature range:

$$n_{s,IN}(T) = \int_{T}^{0} k(T) dT .$$

(2.6)

Using Eq. 2.5 and 2.6 the frozen fraction $FF$ can be expressed as a function of $T$:

$$FF = \frac{N_{i,j}}{N_{tot,j}} = 1 - \exp(-A_{j} \cdot n_{s,IN}(T)) \approx A_{j} \cdot n_{s,IN}(T).$$

(2.7)

The approximation is valid for $A_{j} \cdot n_{s,IN}(T) \ll 1$, which translates into small particles and high temperatures. For low temperatures, e.g. 243.15 K and particles larger than 3 µm the term $A_{j} \cdot n_{s,IN}$ is approximately 1 ($FF \rightarrow 1$).

The surface site density of ice active sites, $n_{s,IN}(T)$, is calculated from the total surface area.
of aerosol particles in the AIDA chamber and the measured ice crystal number concentration during one freezing experiment:

\[
\sum_{j=1}^{n} N_{i,j} \approx \sum_{j=1}^{n} N_{tot,j} \cdot A_j \cdot n_{s,IN}(T) = n_{s,IN}(T) \cdot \sum_{j=1}^{n} N_{tot,j} \cdot A_j
\]

\[
\Leftrightarrow n_{s,IN}(T) = \frac{\sum_{j=1}^{n} N_{i,j}}{\sum_{j=1}^{n} N_{tot,j} \cdot A_j} = \frac{\sum_{j=1}^{n} N_{i,j}}{\sum_{j=1}^{n} A_{tot,j}} \cdot \frac{N_i}{A_{tot}} \tag{2.8}
\]

with \(A_{tot,j}\) the total surface area per unit volume of particles in the size bin \(j\) and \(A_{tot}\) the total surface area over all size bins. In 16 freezing experiments in the AIDA cloud chamber the ice crystal number concentration, formed by active IN, \(N_i\), was measured as a function of \(T\). The total particle surface area, \(A_{tot}\), was estimated before each experiment and multiplied with a pressure dilution factor.

The evaluation of the results yields the following fit formula for the ice active surface site density of natural dust:

\[
n_{s,IN}(T) \left[ m^{-2} \right] = b \cdot \exp(-0.517 \cdot a \cdot (T - 273.15 \, K) + 8.934) , \tag{2.9}
\]

with the fit parameters \(A = -0.517\) and \(B = 8.934\) and the unit correction factors \(a = K^{-1}\) and \(b = m^{-2}\). Due to the temperature range of the freezing experiments, the parameterization is limited to the temperature range from 261.15 K to 237.15 K.

Generally, this scheme distinguishes the freezing behavior of different aerosol species (if different \(n_{s,IN}(T)\) are defined) and takes into account the sizes of the particles. However, it neglects the stochastic nature of the freezing process.
2.3 Theoretical parameterization schemes: the Chen et al. parameterization

Chen et al. developed a parameterization based on CNT (see chapter 3 and 4) to study freezing processes in mixed-phase clouds. The scheme was successfully implemented into the Community Atmosphere Model (CAM)-Oslo GCM by Hoose et al.

The key idea of this parameterization scheme is to follow CNT in combination with experimental data to constrain thermodynamic and kinetic parameters of CNT. The scheme can be used for immersion freezing and deposition nucleation. The freezing rate is determined as a function of $T$, $S$, $t$, size, and type of aerosol particles. Necessary input parameters to be able to calculate the freezing rate are the activation energy $\Delta g^\#$ and the contact angle $\alpha$ of each specific IN (see more details in chapter 3 and 4). Different properties of IN can be included in the contact angle $\alpha$. The parameters can be obtained from experimental data. In Chen et al. (2008) this is done by using a linearized equation of the nucleation rate $J$ and by performing data fitting of the measurement data.

Since CNT is only a framework and not a constrained theory, the theoretical approach needs the input from experimental data and is therefore restricted to the availability of measurements and measurement conditions.

The theoretical foundation (CNT) is explained very detailed in chapters 3 and 4 and therefore not further elaborated here. More details about the parameterization scheme can be found in chapter 5.
Classical nucleation theory: introduction and sensitivity of homogeneous freezing to thermodynamic and kinetic parameters

The probability of homogeneous ice nucleation under a set of ambient conditions can be described by nucleation rates using the theoretical framework of Classical Nucleation Theory (CNT). This framework consists of kinetic and thermodynamic parameters, of which three are not well-defined (namely the interfacial tension between ice and water, the activation energy and the prefactor), so that any CNT-based parameterization of homogeneous ice formation is less well-constrained than desired for modeling applications. Different approaches to estimate the thermodynamic and kinetic parameters of CNT are reviewed in this paper and the sensitivity of the calculated nucleation rate on the choice of parameters is investigated. We show that nucleation rates are very sensitive to this choice. The sensitivity is governed by one parameter—the interfacial tension between ice and water, which determines the energetic barrier of the nucleation process. The calculated nucleation rate can differ by more than 25 orders of magnitude depending on the choice of parameterization for this parameter. The second most important parameter is the activation energy of the nucleation process. It can lead to a variation of 16 orders of magnitude. By estimating the nucleation rate from a collection of droplet freezing experiments from the literature, the dependence of these two parameters on temperature is narrowed down. It can be seen that the temperature behavior of these two parameters assumed in literature does not match with the predicted nucleation rates from the fit in most cases. Moreover, a comparison of all possible combinations of theoretical parameterizations of the dominant two free parameters show that one combination fits the fitted nucleation rates best, which is a description of the interfacial tension coming from a molecular model (Reinhardt and Doye, 2013) in combination with an activation energy derived from self-diffusion measurements (Zobrist et al., 2007). However, some fundamental understanding of the processes is still missing. Further research in future might help to tackle this problem. The most important questions which need to be answered to constrain CNT are raised in this study.

Introduction

Since the first freezing experiments of Fahrenheit in 1753, many studies have elaborated the phase transition of supercooled water. Various experiments revealed that the freezing temperature of pure water droplets has a strong dependence on the droplet size. While droplets 1 cm in diameter freeze at 240 K, 1 µm droplets remain liquid down to 233 K. To a smaller extent exposure time of droplets at a certain temperature influences the probability of droplet freezing. A higher cooling rate also lowers the freezing temperature for a given droplet size. These observations can be well captured by Classical Nucleation Theory (CNT; here CNT always refers to Classical Nucleation Theory of freezing and not nucleation of particles from the gas phase), where the freezing process is described stochastically based on thermodynamic and kinetic parameters (Volmer and Weber, 1926).

When CNT was initially developed, our knowledge about supercooled water and its characteristics was not sufficient (Pruppacher, 1995). Even today, there is still no complete physical model for liquid water, which takes into account all its unusual properties (Jeffery and Austin, 1997) to constrain the theory. Therefore, there are thermodynamic and kinetic parameters in CNT where a comprehensive description is not available or at least not known over a broad temperature range. These unconstrained parameters are a major source of uncertainties in the nucleation rates derived by CNT. As an example, the interfacial tension between water and ice, $\sigma_{iw}$, has not been measured below 273.15 K. This introduces major uncertainties in the energy barrier $\Delta G$.

To reconcile CNT with the outcome of laboratory measurements, several approximations of thermodynamic and kinetic parameters have been proposed on the basis of indirect measurements or theoretical considerations (Türkmen, 2007). On the one hand, studies have focused on kinetics by adapting the kinetic prefactor, e.g. Hagen et al. (1981), Pruppacher (1995) and Huang and Bartell (1995), and on the other hand focused on thermodynamics by changing the interfacial free energy, e.g. Eadie (1971). These different approaches have led to multiple formulations of the unconstrained CNT parameters and the theory itself.

The aim of this paper is to clarify and compare different formulations of CNT currently used in the research community. CNT is used in different research fields with many applications, e.g. biology, food industry and atmospheric sciences (Zettlemeyer, 1969). The focus will be on atmospheric applications in this study. However, the theory itself and findings might also be important for other fields.

The freezing of small water droplets has a major influence on atmospheric cloud formation and the physical properties of clouds. Three major cloud types can be defined in terms of phase: i) water clouds, consisting of water droplets only, ii) mixed-phase clouds, consisting of both ice and water particles, and iii) ice clouds, consisting of ice crystals. Ice in clouds may form
3.1 Classical Nucleation Theory

via homogeneous or heterogeneous ice nucleation mechanisms, depending on the temperature and supersaturation. In the absence of sufficient ice nuclei homogeneous nucleation is the dominant process in cirrus clouds as well as anvils of deep convective clouds at low temperature conditions. Heterogeneous nucleation is the dominant process for mixed-phase clouds and is initiated above the homogeneous freezing temperature (approx. 235 K) by impurities in the water droplets. Comprehensive definitions of heterogeneous nucleation mechanisms can be found in [Vali (1985b)]. However, the focus of this study is on homogeneous nucleation.

The net radiative effect of a cloud depends on its physical properties like temperature, vertical and horizontal extent, optical thickness and phase and is therefore sensitive to freezing processes. The analysis presented in this study will help to develop CNT-based parameterizations of freezing in regional and global climate models to improve the representation of cirrus clouds and anvil formation of deep convective clouds.

In the following section 3.1 the formalism of CNT and the thermodynamic and kinetic concepts making up CNT are introduced before sections 3.2 and 3.3 examine the different thermodynamic and kinetic parameters and summarize the physical considerations or assumptions they are based on. The associated uncertainties are discussed in detail in section 3.4. In section 3.5 we compare CNT, using the parameterizations for the thermodynamic and kinetic parameters as proposed by different authors, to measured homogeneous nucleation rates from 33 droplet freezing experiments using a variety of experimental techniques (Table 3.4). This comparison enables to check the validity of different theoretical estimates of the two most important unconstrained parameters. This gives an indication which formulations are able to quantitatively reproduce laboratory data.

3.1 Classical Nucleation Theory

The key concepts and equations of CNT are summarized here. For details we refer to [Volmer and Weber (1926), Turnbull and Fisher (1949), Fletcher (1962), Dufour and Defay (1963), Young (1993), Debenedetti (1996), Pruppacher and Klett (2000) and references therein. Statistical fluctuation of molecules in supercooled liquid due to thermal vibrations can lead to spontaneous formation of ordered solid molecule clusters, called ice embryos. The size of an embryo fluctuates as individual water molecules (monomers) are gained or lost from liquid phase. However, at a certain critical embryo size additional incorporation of further water molecules to the crystal lattice becomes thermodynamically favored. This critical embryo (ice germ) may then allow the entire parent phase (supercooled liquid) to undergo a macroscopic phase transition: the droplet freezes.

CNT aims to describe this freezing process theoretically, in terms of a temperature-dependent nucleation rate $[m^{-3} s^{-1}]$ by a thermodynamic and a kinetic component (i.e. the temperature
and pressure dependent energy barrier of spontaneous cluster formation and the rate of molecule incooperation into existing clusters. This nucleation rate can be understood as the formation rate of ice germs in a volume of water leading to freezing over time.

### 3.1.1 Thermodynamics of nucleation

The thermodynamic part of the nucleation rate gives the number of ice germs formed per unit volume of water at a given temperature. The formation of a spherical ice embryo in the liquid phase requires a decrease in entropy, and may form a barrier to nucleation. The corresponding change in Gibbs energy required to form an ice embryo containing \( n_k \) water molecules (\( \Delta G_k \)) forms an energy barrier to nucleation. This barrier must be overcome when creating a spherical ice embryo in the liquid phase. It consists of a volume term and a surface term and can be derived by integrating the first law of thermodynamics for the thermodynamic potential \( G \) giving the following expression:

\[
\Delta G_k = \frac{n_k \cdot \left[ \mu_i(T) - \mu_w(T) \right]}{\text{volume term}} + \frac{4\pi r_{\text{embryo}}^2 \sigma_{\text{iw}}(T)}{\text{surface term}},
\]

where \( n_k \) is the number of water molecules in the ice embryo, \( \mu_{w,i}(T) \) the chemical potential of the water/ice phase as a function of temperature, \( r_{\text{embryo}} \) the radius of an assumed-spherical ice embryo (discussed further below) and \( \sigma_{\text{iw}} \) denotes the interfacial tension between ice and water. The first term in Eq. (3.1) (volume term) describes the decrease in chemical potential experienced by the embryo, relative to the parent phase due to the phase transition. This decrease can be expressed as a function of temperature and supersaturation with respect to ice \( (S_i) \):

\[
\mu_i(T) - \mu_w(T) = -k_B T \ln \left( \frac{e_{\text{sw}}(T)}{e_{\text{si}}(T)} \right) = -k_B T \cdot \ln S_i,
\]

where \( k_B \) is the Boltzmann constant and \( S_i \) denotes the ratio of the saturation vapor pressures over water \( (e_{\text{sw}}) \) and ice \( (e_{\text{si}}) \). The number of water molecules in the ice embryo can be calculated from the ratio of the volume of the embryo and the volume of a water molecule in ice \( [v_{\text{ice}}(T)] \):

\[
n_k = \frac{4\pi}{3} \cdot \frac{r_{\text{embryo}}^3}{v_{\text{ice}}(T)}.
\]

In Eq. (3.3) \( v_{\text{ice}}(T) \) can be calculated from the density of ice, which e.g. can be found as an empirical temperature-dependent function in [Pruppacher and Klett (2000)] [Eq. (3.2)]. Using Eq. (3.2) and Eq. (3.3) the volume term can be expressed as:

\[
n_k \cdot \left[ \mu_i(T) - \mu_w(T) \right] = \frac{4\pi}{3} \cdot \frac{r_{\text{embryo}}^3}{v_{\text{ice}}(T)} \cdot (-k_B T \cdot \ln S_i).
\]
The second term in Eq. (3.1) (surface term) describes the energy needed to form the interface of the embryo. The formulation is based on the assumption that the ice embryo is spherical, with an interfacial tension similar to a macroscopic system [e.g. Anisimov (2003)]. In addition, it is usually assumed that the curvature effect on interfacial tension is neglected by assuming that the curvature radius is considerably larger compared to the molecular dimensions [capillary assumption; Gibbs (1948)]. Especially for small clusters, these assumptions may be violated and are major limitations for CNT.

The critical size of an ice embryo (i.e. germ size) is a function of temperature and supersaturation (or saturation ratio). It has been calculated using two different approaches. In the first, the critical germ radius is defined as the maximum of the energy barrier \( \Delta G \) (i.e. at the equilibrium between the volume and surface term), resulting in

\[
 r_{\text{germ}} = \frac{2 v_{\text{ice}} \sigma_{\text{iw}}}{k_B T \ln \left( \frac{T_0 \cdot (T_0 - T)}{T} \right)}.
\]  

(3.5)

In the second approach, the equilibrium condition for the ice germ in a supercooled droplet of pure water which itself is in equilibrium with humid air [Pruppacher and Klett (2000); Eq. (6.10) and (6.52)] is integrated. This approach becomes equivalent to the first, if the saturation ratio is expressed as a function of the latent heat of melting \( L_m \) [e.g. Rogers and Yau (1989), Eq. (2.15)]:

\[
 S_i = \exp \left( -\frac{L_m}{k_B T} \cdot \frac{T_0 - T}{T} \right),
\]  

(3.6)

where \( T_0 = 273.15 \) K.

Other formulations for \( r_{\text{germ}} \), taking solution and curvature effects into account, can for example be found in Khvorostyanov and Sassen (1998), Khvorostyanov and Curry (2000) and Jeffery and Austin (1997).

Eqs. (3.4) and (3.5) can be inserted into Eq. (3.1) to predict the energy barrier \( \Delta G \) to ice germ formation as:

\[
 \Delta G = \frac{16\pi}{3} \cdot \frac{v_{\text{ice}}^2 \sigma_{\text{iw}}^3}{(k_B T \ln S_i)^2}.
\]  

(3.7)

The temperature and saturation dependent number of ice germs \( N_{\text{germ}} \) per unit volume of water can be expressed in form of a Boltzmann distribution using \( \Delta G \) [Eq. (3.7)]:

\[
 N_{\text{germ}} [\text{m}^{-3}] = N_l \cdot \exp \left( -\frac{\Delta G}{k_B T} \right),
\]  

(3.8)

where \( N_l \) is the volume-based number density of water molecules in the liquid parent phase.
### 3.1.2 Kinetics of nucleation

The kinetic part of the nucleation rate gives the number of water molecules, which can potentially be incorporated into the ice germ. The flux of water molecules available for incorporation into an ice germ must be taken into account in order to estimate a nucleation rate. This flux can be understood as the diffusive flux ($\Phi$), which can be expressed as a Boltzmann distribution:

$$\Phi = \frac{k_B T}{h} \cdot \exp\left(\frac{\Delta g^a}{k_B T}\right),$$  \hspace{1cm} (3.9)

where $h$ denotes the Planck’s constant and $\Delta g^a$ the activation energy for the transfer of a water molecule across the water-ice boundary [cf. section 3.2.1, Eq. (3.14)-(3.16)]. $\Phi$ can be interpreted either as the frequency at which water molecules overcome the activation energy barrier (Balibar and Caupin, 2006), as a rate of collisions or as a probability of bond breaking and molecular reorganisation (Pruppacher and Klett, 2000).

A second kinetic prefactor, the Zeldovich factor $Z$, accounts for the depletion of the cluster population due to germ production (Zeldovich, 1942). This factor embodies the non-equilibrium of the kinetic process and has a value between $10^{-2}$ and 1, where a value of 1 means that equilibrium is assumed. The estimation of $Z$ is discussed further in section 3.2.2.

Using the described expressions for the diffusive flux $\Phi$ and the kinetic prefactor $Z$ the rate $K$ at which water molecules are transferred into an ice germ can be predicted by

$$K = n_s \cdot 4\pi r^2_{\text{germ}} \cdot Z \cdot \Phi,$$  \hspace{1cm} (3.10)

where $n_s$ is the number of molecules in jumping distance around the germ surface/neighbor the germ surface and $4\pi r^2_{\text{germ}}$ is the surface area of the critical ice germ (see section 3.2.2).

### 3.1.3 Nucleation rate

Combining the thermodynamic [Eq. (3.8)] and the kinetic part [Eq. (3.10)], a formulation of the steady state nucleation rate can be expressed as:

$$J_{\text{hom}}[\text{m}^{-3} \cdot \text{s}^{-1}] = K_{\text{Kinetics}} \cdot \frac{N_l \cdot \exp\left(-\frac{\Delta G}{k_B T}\right)}{\text{Number of germs}},$$  \hspace{1cm} (3.11)

Inserting Eq. (3.10) and Eq. (3.9) into Eq. (3.11) leads to:

$$J_{\text{hom}}[\text{m}^{-3} \cdot \text{s}^{-1}] = n_s \cdot 4\pi r^2_{\text{germ}} \cdot Z \cdot \Phi \cdot N_l \cdot \exp\left(-\frac{\Delta G}{k_B T}\right).$$
3.2 Uncertainties in the kinetics

\[ J_{\text{hom}} \left[ m^{-3} \cdot s^{-1} \right] = \frac{C_{\text{prefac}}}{\text{preexp. factor}} \cdot \exp \left( -\frac{\Delta g^\#}{k_B T} \right) \cdot \exp \left( -\frac{\Delta G}{k_B T} \right) \cdot \exp \left( -\frac{\Delta G}{k_B T} \right) \]  

(3.13)

The variables \( N_t, n_s, Z \), the surface area of the ice germ and the prefactor \( k_B T/h \) of the flux \( \Phi \) are summarized as the preexponential factor \( C_{\text{prefac}} \) (see section 3.2.2):

\[ n_s \cdot 4\pi r_{\text{germ}}^2 \cdot Z \cdot \frac{k_B T}{h} \cdot \exp \left( -\frac{\Delta g^\#}{k_B T} \right) \cdot N_t \cdot \exp \left( -\frac{\Delta G}{k_B T} \right) \]  

(3.12)

In sections 3.2 and 3.3 uncertainties associated with the individual unconstrained components of Eq. (3.13) are analyzed and evaluated in section 3.4 and 3.5.

### 3.2 Uncertainties in the kinetics

#### 3.2.1 Activation energy (\( \Delta g^\# \))

The activation energy (\( \Delta g^\# \)) describes the energy required for a single molecule to diffuse across the water-ice boundary, in addition to the free energy barrier \( \Delta G \). \( \Delta g^\# \) can be understood as the activated state through which a molecule must pass when diffusing from the parent phase to the embryo of the new phase (Turnbull and Fisher, 1949). It is difficult to perform direct measurements from which to determine \( \Delta g^\# \). Various estimation methods have been applied and have yielded in diverse findings. Nevertheless, the following independent characteristics of \( \Delta g^\# \) can be stated:

- The diffusion of a water molecule from the liquid phase into the ice lattice requires the breaking of hydrogen bonds between the diffusing water molecule and its neighbors. After breaking loose (one or two hydrogen bonds may be retained) the molecule is influenced by the force field of the surrounding water molecules and moves across the interface. The breaking of hydrogen bonds increases the internal energy of the diffusing water molecule, allowing it to overcome \( \Delta g^\# \) (Bulavin et al., 2008). Therefore \( \Delta g^\# \) depends on the number of hydrogen bonds connecting a given water molecule to its neighbors, which is dependent on the structure of the water (hydrogen bond network of the water molecules). Below 310 K, a water molecule is expected to possess an average of three tetrahedrally-arranged hydrogen bonds (Bulavin et al., 2008).

- As diffusion depends on temperature, so does the activation energy. \( \Delta g^\# \) increases with decreasing temperature, because the average number of hydrogen bonds in a network of
supercooled water molecules increases with decreasing vibrational energy (Pruppacher and Klett 2000). Hydrogen bond strength increases with decreasing temperature and the structure of the water itself becomes more ice-like at lower temperature (Dorsch and Boyd 1951, Fecko et al. 2003). Bulavin et al. (2008) showed that self-diffusion in water is based on the movement of single water molecules (one-particle contribution) near 273.15 K. At low temperatures the collective contribution of self-diffusion might become more important. Therefore, Hagen et al. (1981) proposed a contrary temperature dependence below 241 K. They argue that below this temperature the diffusion process is a cooperative phenomenon and ice embryos grow by transfer of increasingly large water clusters instead of monomers. Consequently less hydrogen bonds – only the ones at the cluster periphery – have to be broken.

There are three measurable quantities (defined by the Glasstone relations (Glasstone et al. 1941, Jeffery and Austin 1997)) based on which the activation energy $\Delta g^\#$ can be estimated: the viscosity of water $\eta$, the self-diffusivity of water $D$ and the dielectric relaxation time $\tau$ of water:

$$\eta = \eta_0 \cdot \exp\left(\frac{\Delta g_\eta^\#(T)}{RT}\right)$$  \hspace{1cm} (3.14)

$$D = D_0 \cdot \exp\left(-\frac{\Delta g_D^\#(T)}{RT}\right)$$  \hspace{1cm} (3.15)

$$\frac{1}{\tau} = \frac{k_B T}{h} \cdot \exp\left(-\frac{\Delta g_\tau^\#}{k_B T}\right).$$  \hspace{1cm} (3.16)

Measurements of Krynicki et al. (1978) showed that $\Delta g_\eta^\#$ and $\Delta g_D^\#$ are around $19 \cdot 10^3$ J mol$^{-1}$ near the melting point. Wang et al. (1953) estimated $\Delta g_\eta^\#, \Delta g_D^\#$ and $\Delta g_\tau^\#$ at 298.15 K and proposed that the activation barrier is the same for viscous flow, self-diffusion and dipole orientation with breaking approximately two hydrogen bonds. However, it has not been proven that all three relations are physically correct, nor that $\Delta g_\eta^#, \Delta g_D^#, \Delta g_\tau^#$ are equal. The possibility of $\Delta g^\#$ depending on the measured quantity is beyond the scope of this work. Thus $\Delta g^\#$ is used in the following for the activation energy independent of the measurable quantity the estimation is based on.

The value of $\Delta g^\#$ derived from different analyses varies with the input data as well as the applied fitting method. Eight different descriptions of $\Delta g^\#$ from Dufour and Defay (1963), Eadie (1971), Young (1993), Pruppacher and Klett (2000), Jeffery and Austin (1997), Zobrist et al. (2007), Chen et al. (2008) and the extension of the Pruppacher and Klett (2000) formulation from Khvorostyanov and Curry (2000) are shown in Fig. 3.1 as a function of temperature. The methods and datasets used are summarized in Table 3.1 and described in detail in Appendix 3.A.
3.2 Uncertainties in the kinetics

Figure 3.1: Variation of the activation energy $\Delta g^\#$ with temperature $T$. Figure modified from Hoose and Möhler (2012). Note that the curve 6 shows only the extension for low temperatures by Khvorostyanov and Curry (2000) (see Appendix 3.A).

<table>
<thead>
<tr>
<th>Theory</th>
<th>$\Delta g^#$ based on</th>
<th>Dataset</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dufour &amp; Defay 1963</td>
<td>viscosity</td>
<td>Huber et al. 2009;</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Collie et al. 1948</td>
<td></td>
</tr>
<tr>
<td>Eadie 1971</td>
<td>dielectric relaxation time</td>
<td>Hallett</td>
<td></td>
</tr>
<tr>
<td>Young 1974</td>
<td>viscosity and homogeneous</td>
<td>Hagen and Anderson 1981</td>
<td></td>
</tr>
<tr>
<td></td>
<td>freezing data</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jeffery &amp; Austin 1997</td>
<td>self-diffusivity</td>
<td>Prielmeier et al. 1987; Harris and Wolf</td>
<td></td>
</tr>
<tr>
<td>Khvorostyanov &amp; Curry 2000</td>
<td>homogeneous freezing data</td>
<td>similar to Jensen et al. 1994</td>
<td>$T &lt; 243.15$ K</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Hagen et al. 1981; DeMott and Rogers 1990)</td>
<td></td>
</tr>
<tr>
<td>Zobrist et al. 2007</td>
<td>see Pruppacher &amp; Klett</td>
<td>Smith and Kay 1991</td>
<td>$T &gt; 243.15$ K</td>
</tr>
<tr>
<td>Chen et al. 2008</td>
<td>self-diffusivity fitting parameter</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.1: Summary of methods for estimating $\Delta g^\#$

The different $\Delta g^\#$ in Fig. 3.1 spread over almost one order of magnitude. This spread leads to an even larger variation in the predicted nucleation rate $J_{\text{hom}}$, as $\Delta g^\#$ is found in the exponential term of Eq. (3.9). Notably, the expression of Khvorostyanov and Curry (2000) has an opposite
temperature dependence to the other formulations below 243.15 K, so that the difference in $\Delta g^\#$ is the largest in this temperature regime. This difference can be traced to a lack of understanding of the change in water structure bonding at low temperatures.

### 3.2.2 Prefactor ($C_{\text{prefac}}$)

In this section the different values of the variables comprising $C_{\text{prefac}}$, which is the prefactor in front of the energy barriers in Eq. (3.13), are listed. We emphasize that the definition of $C_{\text{prefac}}$ is not the same definition as used by all authors. Moreover, some authors estimated $C_{\text{prefac}}$ as a single quantity to simplify the calculation. The sensitivity of $J_{\text{hom}}$ to the parameters discussed in this section is evaluated in section 3.4.

**Number of water molecules in contact with the unit area of an ice germ ($n_s$) and volume number density of water molecules in liquid water ($N_l$).**

$n_s$ has been estimated as a temperature-independent value by different authors between $5.85 \cdot 10^{18}$ m$^{-2}$ and $1 \cdot 10^{19}$ m$^{-2}$. See Appendix 3.B for details.

The factor $N_l$ accounts for the fact that homogeneous nucleation is a volume dependent process. The variation of this parameter in literature estimates is not as large as in the case of $n_s$. In Tabazadeh et al. (2002), the number density of water molecules in a solution droplet of 1 m$^{-3}$ is given as $3.35 \cdot 10^{28}$ m$^{-3}$ consistent with Jacobi (1955), who reported $3.33 \cdot 10^{28}$ m$^{-3}$, whereas in Zobrist et al. (2007) a slightly lower value of $3.1 \cdot 10^{28}$ m$^{-3}$ is used.

**Zeldovich factor ($Z$).**

$Z$ represents the non-equilibrium nature of an ice-nucleating system (i.e. ice embryos plus parent phase). It accounts for the loss of subcritical clusters in the embryo population due to the growth of ice embryos, which reduces the number of water molecules available to transfer across the water-ice interface. If an equilibrium is assumed, $Z$ has the value 1. Otherwise, $Z$ can be estimated as follows:

$$Z = \frac{1}{n_{k, \text{germ}}} \cdot \sqrt{\frac{\Delta G}{3\pi k_B T}}. \quad (3.17)$$

Whereas Fletcher (1962) states that the effect of taking $Z$ into account is minor, Pruppacher and Klett (2000) reckon that $Z$ has the order of $10^{-1}$ and Butorin and Skripov (1972) estimate $Z$ to be of the order of $10^{-2}$.  

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3.3 Uncertainties in the thermodynamics

Estimates of the total prefactor $C_{\text{prefac}}$

By coincidence, the product of $n_s$, the germ surface area $A$, and $Z$ is approximately equal to unity. Therefore the total prefactor is approximately the product of the volume number density $N_l$ and the temperature dependent term $k_B T/\hbar$. Fletcher (1962), Young (1993) and Debenedetti (1996) for example approximate the prefactor for homogeneous freezing by $10^{41} \text{m}^{-3} \text{s}^{-1}$ over the whole temperature range.

3.3 Uncertainties in the thermodynamics

3.3.1 Interfacial tension between ice and water ($\sigma_{iw}$)

The interfacial tension between ice and water ($\sigma_{iw}$) is an important but poorly-constrained parameter in CNT [cf. Eq. (3.7)]. $\sigma_{iw}$ is strongly temperature-dependent, due to the temperature dependence of the structure of water. With decreasing temperature, the structure of water becomes increasingly ice-like (Dorsch and Boyd, 1951, Fecko et al., 2003), decreasing the ice-water interfacial entropy (ordering of water molecules in contact with the ice structure increases) and thus $\sigma_{iw}$. The interfacial free energy, and thus the interfacial entropy, becomes zero in the limiting case where the water structure is completely isomorphic with ice (McDonald, 1953).

Direct measurements of $\sigma_{iw}$ for ice embryos is nearly impossible, as they may be smaller than 1 nm (Zobrist et al., 2007). Moreover, metastable supercooled water tends to freeze heterogeneously on any experimental apparatus. Therefore, $\sigma_{iw}$ is normally measured at or above 273.15 K using macroscopic water drops. These measurements are then extrapolated to ice embryos in supercooled water. This approach implicitly assumes that the ice embryos have the same intensive properties as bulk water. In addition, the extrapolation of $\sigma_{iw}$ to supercooled temperatures requires theoretical assumptions about its temperature dependence. These assumptions introduce significant uncertainty to the result. Alternatively, the interfacial tension between ice and water can be estimated by using molecular models or based on fitting of CNT to measured nucleation rates.

Several different estimates of $\sigma_{iw}$ are summarized in Fig. 3.2 as a function of temperature. The figure includes measurements of $\sigma_{iw}$ at 273.15 K ($\sigma_{iw,0}$) and their theoretical extrapolations as just described, theoretical estimates of $\sigma_{iw,0}$ and $\sigma_{iw}(T)$, as well as results from molecular models and results from fits of CNT. Table 3.2 gives the methods and datasets used in each of these studies. See Appendix 3.C and 3.D for more details.
Figure 3.2: Variation of the interfacial tension $\sigma_{iw}$ with temperature $T$ and measurements of $\sigma_{iw}$. Solid lines indicate estimates based on fits to nucleation measurement data, dashed lines indicate theoretical estimates, dotted lines results from molecular models. The macroscopic measurement results at the right hand side of the plot are all (besides the value of Kubelka and Prokscha (1944)) measured at 273.15 K but plotted on a slightly wider temperature range to enable identification of the single points. They are shown by full circles (●), open diamonds (◇), crosses (×), and stars (*). The error bars of the points from Skapski et al. (1957) and Jones and Chadwick (1970) are symmetric (upper limits are not shown completely). The open circled points (○) show results from molecular simulations, plus signs (+) from theoretical estimates, and open squares (□) estimates resulting from nucleation measurements.
### 3.3 Uncertainties in the thermodynamics

<table>
<thead>
<tr>
<th>Theory</th>
<th>$\sigma_{iw}$ based on</th>
<th>Dataset</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young relation 1805</td>
<td>equilibrium of interfacial tensions</td>
<td>Pruppacher &amp; Klett 1997, Hale &amp; Plummer 1974</td>
</tr>
<tr>
<td>Ouchi 1954</td>
<td>thermodynamic concept</td>
<td>-</td>
</tr>
<tr>
<td>Jacobi 1955</td>
<td>nucleation measurements</td>
<td>Jacobi 1955</td>
</tr>
<tr>
<td>Dufour &amp; Defay 1963</td>
<td>nucleation measurements</td>
<td>Wood &amp; Walton 1970</td>
</tr>
<tr>
<td>Wood &amp; Walton 1970</td>
<td>nucleation measurements</td>
<td>-</td>
</tr>
<tr>
<td>Eadie 1971</td>
<td>statistical concept</td>
<td>Taborek 1985</td>
</tr>
<tr>
<td>Taborek 1985</td>
<td>nucleation measurements</td>
<td>DeMott &amp; Rogers 1990</td>
</tr>
<tr>
<td>Pruppacher &amp; Klett 1997</td>
<td>thermodynamic concept</td>
<td>unpublished</td>
</tr>
<tr>
<td>Jeffery &amp; Austin 1997</td>
<td>thermodynamic concept (Turnbull 1950)</td>
<td>-</td>
</tr>
<tr>
<td>Gránásy et al. 2002</td>
<td>nucleation measurements + continuum model</td>
<td>Taborek 1985</td>
</tr>
<tr>
<td>Chukin et al. 2010 (233 - 273 K)</td>
<td>similar as Pruppacher &amp; Klett</td>
<td>-</td>
</tr>
<tr>
<td>Murray et al. 2010</td>
<td>nucleation measurements</td>
<td>Murray et al. 2010</td>
</tr>
<tr>
<td>Reinhardt &amp; Doye 2013</td>
<td>molecular model (TIP4P)</td>
<td>-</td>
</tr>
<tr>
<td>Sanz et al. 2013</td>
<td>TIP4P in combination with CNT</td>
<td>-</td>
</tr>
</tbody>
</table>

**Table 3.2: Summary of methods for estimating $\sigma_{iw}$**

$\sigma_{iw}$ differs by up to a factor of three (Fig. 3.2) and follows differing temperature trends. It can be described in terms of two components: the magnitude of its value at the melting point ($\sigma_{iw,0}$) and its temperature dependence. Literature estimates of $\sigma_{iw}$ vary between $10 \cdot 10^{-3}$ and $44 \cdot 10^{-3}$ J m$^{-2}$ at 273.15 K, and between $6.8 \cdot 10^{-3}$ and $26.7 \cdot 10^{-3}$ J m$^{-2}$ at 220 K. As noted above, $\sigma_{iw}$ is expected to decrease with temperature. Most of the theoretical and molecular-modeling approaches suggest that this decrease should be linear, with a slope between 0.1 and $0.25 \cdot 10^{-3}$ J m$^{-2}$ K$^{-1}$ (see Table 3.3). The only studies that report a temperature dependence which is very different from a linear dependence is that of Zobrist et al. (2007), where a function was fitted to experimental nucleation rate data without theoretical consideration, the Young relation by Pruppacher and Klett (2000), where $\sigma_{iw}$ was constrained by the singularity behavior of water at 228.15 K.

Describing $\sigma_{iw}$ is a challenging task due to the spread of available measurement data at the melting point (see Fig. 3.2) and the unknown temperature behavior. In Fig. 3.3, the importance
of the reference value $\sigma_{iw,0}$ versus the importance of the predicted temperature dependence is examined. The figure shows the temperature-dependent functions reported in the literature for a single value of $\sigma_{iw,0}$. The measured $\sigma_{iw,0}$ of Hardy \cite{Hardy1977} was taken as the reference value, in accordance with current consensus \citep[see e.g.,][]{Granasy2002}. With an unified reference value, better agreement than Fig. 3.2 can be seen (narrower range of values for $\sigma_{iw}$ on the ordinate). However, significant spread remains.

It is interesting to compare the results from molecular models with other estimates. The molecular-model results are fundamentally different from others, as the molecular mechanics of water molecules building clusters is explicitly simulated. Fig. 3.2 shows that these molecular modeling results are within the uncertainty range of Hardy \cite{Hardy1977} at 273.15 K \citep[besides the value of][]{Digilov2004}. Additional information from sophisticated molecular models may be able to reduce the uncertainty in $\sigma_{iw}(T)$ in future. Nevertheless, the spread of the results reported is still quite large.

![Figure 3.3: Variation of the interfacial tension $\sigma_{iw}$ with temperature $T$ shifted to the measurement point of Hardy \cite{Hardy1977}. Solid lines indicate estimates based on fits to nucleation measurement data, dashed lines indicate theoretical estimates, dotted lines results from molecular models.](image-url)
3.4 Sensitivity analysis

<table>
<thead>
<tr>
<th>Theory</th>
<th>$\sigma_{iw,0}$ [10^{-3} \text{ J m}^{-2}]</th>
<th>$d\sigma_{iw}/dT$ [10^{-3} \text{ J m}^{-2} \text{ K}^{-1}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jacobi 1955</td>
<td>23.07 (extrapolated)</td>
<td>0.2</td>
</tr>
<tr>
<td>Dufour &amp; Defay 1963</td>
<td>23.8 (extr.)</td>
<td>0.102</td>
</tr>
<tr>
<td>Wood &amp; Walton 1970</td>
<td>31.93 ± 0.44 (extr.)</td>
<td>0.211 ± 0.012</td>
</tr>
<tr>
<td>DeMott &amp; Rogers 1990</td>
<td>28</td>
<td>0.167</td>
</tr>
<tr>
<td>Taborek 1985</td>
<td>32 (extr.)</td>
<td>0.1</td>
</tr>
<tr>
<td>Pruppacher &amp; Klett 1997</td>
<td>28</td>
<td>0.25</td>
</tr>
<tr>
<td>(237.15 K-273.15 K)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gránásy et al. 2002</td>
<td>28.5 (extr.)</td>
<td>0.1</td>
</tr>
<tr>
<td>Chukin et al. 2010</td>
<td>28.5</td>
<td>0.25</td>
</tr>
<tr>
<td>Reinhardt &amp; Doye 2013</td>
<td>30 (extr.)</td>
<td>0.18</td>
</tr>
<tr>
<td>Sanz et al. 2013</td>
<td>28.7</td>
<td>0.18</td>
</tr>
</tbody>
</table>

Table 3.3: Values from linear parameterizations of $\sigma_{iw}(T)$

3.3.2 Saturation ratio

Another parameter included in the calculation of the nucleation rate is the saturation ratio [see Eq. (3.2)]. Murphy and Koop (2005) have investigated the spread of results obtained by different parameterizations for the saturation ratio. Different formulations are in good agreement above 238.15 K, but may become significantly different at lower temperatures. Moreover, the recent study of Murray et al. (2010) shows that assuming the ice structure to be cubic instead of hexagonal changes the saturation ratio with respect to ice and $\sigma_{iw}$ significantly, when estimated from nucleation measurements. Between 180 and 190 K the vapor pressure is 10.5% ± 2.5% larger for cubic ice compared to hexagonal ice. The difference gets smaller with higher temperatures (8.3% at 235 K).

The sensitivity of the nucleation rate to the calculation of the saturation vapor pressure with respect to water and ice as well as the difference between cubic and hexagonal ice is not investigated here. Most studies cited here are based on the assumption of hexagonal ice, so that the saturation ratio was calculated for this ice type based on Goff (1957) as recommended by the World Meteorological Organization (2000).

3.4 Sensitivity analysis

In this section, the sensitivity of CNT to different parameters, parameterizations, and assumptions is analyzed by plotting the nucleation rate $J_{\text{hom}}$ as a function of temperature. $J_{\text{hom}}(T)$ is plotted for each parameter discussed in sections 3.2 and 3.3. Figure 3.4 shows that the nucleation rate $J_{\text{hom}}$ is smaller when a high value of $\Delta g^\gamma$ is chosen, as the kinetic barrier for cluster formation thus becomes larger. Depending on the choice of $\Delta g^\#, the predicted nucleation rate at 230 K differs by up to 16 orders of magnitude. This difference does not translate directly to
a disagreement between the studies cited in Fig. 3.4 as some CNT formulations have estimated Δ$g^\#$ based on other free parameters. For example, $\sigma_{iw}$ has been kept the same [based on Pruppacher and Klett (2000)] for all calculations in Fig. 3.4 but different values were originally used by the authors of those studies.

To examine the influence of the prefactor $C_{\text{prefac}}$ on the nucleation rate, the number of water molecules in contact with the unit area of the ice germ $n_s$ and the volume number density of water molecules in liquid water $N_l$ were varied. Additionally importance of the Zeldovich factor was investigated. As can be seen in Fig. 3.5 the spread of reported literature values for $n_s$ and $N_l$ do not lead to a large spread in $J_{\text{hom}}$ compared to the influence of the choice of other unconstrained parameters.

Accounting for the Zeldovich factor $Z$ reduces the total nucleation rate in a manner dependent on the formulation used for $r_{\text{germ}}$ [Eq. (3.5)] and $\sigma_{iw}$, as $\Delta G$ [Eq. (3.1)] and $n_k,germ$ are part of the formula for $Z$ [see Eq. (3.17)]. This dependence complicates the comparison and makes a
3.4 Sensitivity analysis

Figure 3.5: Variation of the nucleation rate $J_{\text{hom}}$ in dependence of the temperature $T$ due to the choice of the water molecules in contact with the unit area of the ice germ $n_s$ (in this case $N_l$ is kept constant) and the volume number density of water molecules in liquid water $N_l$ (in this case $n_s$ is kept constant) compared to the use of an approximated total prefactor $C_{\text{prefac}}$. In addition the difference in taking into account the Zeldovich factor is shown. To increase the clarity of the figure only the cases with largest differences are chosen (lines which were to similar were left out). For the interfacial tension $\sigma_{iw}$ the formulation of Pruppacher and Klett (2000) is used (see section 3.3.1), the activation energy $\Delta g^*$ is kept constant at $14.5 \times 10^{-20}$ J.

A comprehensive statement about the sensitivity of the nucleation rate caused by accounting versus non-accounting ($Z=1$) of the Zeldovich factor impossible. In this example, using the formulation of $\sigma_{iw}$ by Pruppacher and Klett (2000) lowers $J_{\text{hom}}$ by two orders of magnitude in comparison to setting $Z = 1$.

The difference between the detailed calculation of the prefactor $C_{\text{prefac}}$ and using an approximated temperature independent prefactor as suggested by Fletcher (1962) and Young (1993) is max. two orders of magnitude.
Figure 3.6: Variation of the energy barrier $\Delta G$ with temperature $T$ due to the choice of the interfacial tension $\sigma_{iw}$. Solid lines indicate estimates based on fits to nucleation measurement data, dashed lines indicate theoretical estimates, dotted lines results from molecular models.

Figure 3.6 shows the variation of the energy barrier $\Delta G$ due to the choice of $\sigma_{iw}$. Fig. 3.7 shows the corresponding variation in the nucleation rate. The nucleation rate can differ by around 25 orders of magnitude at 230 K (Fig. 3.7), which is larger than the spread due to the choice of $\Delta g^\#$ (16 orders of magnitude). Again, a direct comparison is difficult because there are interdependencies in the estimation of the different parameters in some studies. Therefore, Fig. 3.7 shows one example for a constant $\Delta g^\#$ based on Chen et al. (2008) and one for $\Delta g^\#(T)$ based on Jeffery and Austin (1997). The spread of $J_{\text{hom}}$ is approximately the same in both cases, providing evidence that $\sigma_{iw}$ is the dominant factor controlling the shape of the curve of $J_{\text{hom}}(T)$.

The nucleation rate $J_{\text{hom}}(T)$ is governed by the exponential terms in the equation. The steepness of $J_{\text{hom}}(T)$ is dominated by the thermodynamic exponent, indicating that $\sigma_{iw}$ is the controlling factor of $J_{\text{hom}}(T)$ (see Fig. 3.8). The kinetic exponent is more important at very low temperatures, where the energetic barrier of the freezing process becomes small enough that the process is limited by kinetics.

The sensitivity studies also show that the choice of $\sigma_{iw}$ and $\Delta g^\#$ influences the calculated nucleation rate considerably whereas the choice of the prefactor, respectively the components of $C_{\text{prefac}}$ does not matter so much for $J_{\text{hom}}$. Therefore the further focus is on $\sigma_{iw}$ and $\Delta g^\#$ only.
Figure 3.7: Variation of the nucleation rate $J_{\text{hom}}$ in dependence of the temperature $T$ due to the choice of the parameterization of the interfacial tension $\sigma_{\text{iw}}$ using (a) a constant activation energy $\Delta g^\#$ of $14.5 \cdot 10^{-20} \text{ J}$ or (b) a temperature dependent activation energy $\Delta g^\#(T)$ based on Jeffery and Austin (1997). The prefactor $C_{\text{prefac}}$ was assumed to be constant ($10^{41} \text{ m}^{-3}\text{s}^{-1}$). Note that the nucleation curves shown are not necessarily representing the nucleation curves from the original studies of the authors written in the legend because the formulation of $J$, the formulation of $\Delta g^\#$ or the prefactor could be different.
Note that the spread in the nucleation rate estimates resulting from the choice of $\Delta g^\#$ and $\sigma_{iw}$ depends on the different formulations found in literature and cannot be generalized from Fig. 3.4 and Fig. 3.7. Therefore in section 3.4.1 the sensitivity on the parameters was investigated independent of the different formulations in the literature.

### 3.4.1 Uncertainty of using CNT

To illustrate the uncertainty resulting from the choice of the different formulations of CNT parameters, the relative error in the nucleation rate was estimated by varying the free parameters $\sigma_{iw}$ and $\Delta g^\#$ within $\pm$ 50% from one estimate values (Fig. 3.9). The calculations were done at 243 K and at 233 K, as this is a temperature range around the onset of homogeneous freezing in atmospheric clouds. In Fig. 3.9 it can be seen that in all cases the impact of uncertainties in $\sigma_{iw}$ and $\Delta g^\#$ is not symmetric. $\sigma_{iw}$ is the parameter with the largest uncertainty (dark blue lines), which dominates the uncertainty in $J_{hom}$. For example, at 243 K a minor decrease in $\sigma_{iw}$
of 0.5% leads to an uncertainty in $J_{\text{hom}}$ of 94%. On the other hand, decreasing $\Delta g^\#$ by 0.5% only changes $J_{\text{hom}}$ by 16%. Uncertainties in $\sigma_{\text{iw}}$ have a larger impact on $J_{\text{hom}}$ than uncertainties in $\Delta g^\#$ at higher temperature. Note that in the case of increasing $\sigma_{\text{iw}}$ or $\Delta g^\#$, $J_{\text{hom}}$ decreases (towards the limit of zero) so that the relative change in $J_{\text{hom}}$ for such an increase is always ≤ 100%. In that case the uncertainties approach -100%, which cannot be exceeded.

Looking at the spread in the free parameters estimated by different studies in the literature, it can be seen that an uncertainty of at least 50% is common. This translates into an uncertainty in $J_{\text{hom}}$ of 18 orders of magnitude. In contrast, measured values of $J_{\text{hom}}$ generally differ by six orders of magnitude. A six-orders-of-magnitude uncertainty in $J_{\text{hom}}$ translates into an uncertainty in $\sigma_{\text{iw}}$ of 6% at 243 K and 18% at 233 K, and in an uncertainty in $\Delta g^\#$ of 35% for the whole temperature range. Note that the temperature dependence of the uncertainty due to variation of $\Delta g^\#$ is negligible here. With this level of precision, it is not possible to decide which literature formulation of $\sigma_{\text{iw}}$ and $\Delta g^\#$ is the most realistic. Nevertheless, in the next section we try to constrain possible ranges for $\sigma_{\text{iw}}$ and $\Delta g^\#$ from a fitted function of $J_{\text{hom}}$.

Figure 3.9: Magnitude of deviation from a reference ice nucleation rate $J_{\text{hom}}$ in percent (relative uncertainty). The results are shown for a variation of the values of $\sigma_{\text{iw}}$ and $\Delta g^\#$ from (a) 0.01 to 50% in the temperature range of 233 to 243 K (shaded area) and (b) for a variation of 0 to 2% (zoom of (a)).
3.5 Constraining $\sigma_{iw}$ and $\Delta g^#$ with $J_{\text{hom}}$

The sensitivity analysis of section [3.4] shows that it is difficult to evaluate the formulations of $\Delta g^#$ and $\sigma_{iw}$ separately. Additionally, many authors fix one of the parameters (based on theoretical considerations), while the other one is then estimated by fitting plausible freezing rates to experimental data. The choice of the fit parameter influences the values of the other free parameters. Therefore, an estimate of the nucleation rate $J_{\text{hom}}(T)$ will be used here to express $\Delta g^#$ or $\sigma_{iw}$ depending on the different theoretical formulations (see Appendix [3.A] and [3.C]) of either $\sigma_{iw}$ or $\Delta g^#$. By using the whole range of approaches and assumptions, the range of the free parameters can be constrained within the uncertainty limits of $J_{\text{hom}}(T)$. From this analysis a suitable temperature dependence emerges. Moreover, all possible combinations of the different theoretical formulations of $\sigma_{iw}$ and $\Delta g^#$ are explored by using the fit result to appoint the best combination.
3.5 Constraining $\sigma_{iw}$ and $\Delta g^\#$ with $J_{\text{hom}}$

3.5.1 Fitting $J_{\text{hom}}$ to experimental data

A comprehensive dataset of 33 homogeneous freezing measurements was collected and fitted by least-squares minimization using three different approaches, which are explained further on. The dataset consists of measurements from many different experimental setups collected over the last few decades, covering different temperature ranges. An overview of the dataset and the used measurement techniques can be found in chronological order in Table 3.4 and in Figs. 3.10 and 3.11. Table 4 includes information about the temperature uncertainty of the measurement. In Figs. 3.10 and 3.11 the measurement uncertainty of the nucleation rate can be seen. Note that the measurement uncertainty of the nucleation rate does not reflect the uncertainty introduced by experimental parameters, which has been discussed in Riechers et al. (2013). The raw data would be needed to be able to re-evaluate the measurements and evaluate uncertainties. The re-evaluation of the data is beyond the scope of this paper, but important for any future analysis (see section 3.6). On the premise that measurement techniques have got more precise over the years, the dataset was divided almost equally into measurements made before or after the year 2000 (indicated by red and blue colors in Fig. 3.10 and Fig. 3.11). Note that the data from Huang and Bartell (1995), Bartell and Chushak (2003) and Manka et al. (2012) were not measured at atmospheric pressure but at high pressure conditions due to the use of supersonic nozzles. The data were nevertheless included to guide the fitting algorithm in the low temperature regime. In addition to the 33 measurements, the simulated nucleation rates from Sanz et al. (2013) were added to guide the fit in the high-temperature regime (see Table 3.4).
### Dataset Measurement Uncertainty Comments

<table>
<thead>
<tr>
<th>#</th>
<th>Dataset</th>
<th>Measurement technique</th>
<th>Uncertainty range (T)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Schaefer 1952</td>
<td>Cloud chamber</td>
<td>± 0.5 K</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Bigg 1953</td>
<td>Suspension</td>
<td>± 0.5 K</td>
<td>two immiscible liquids</td>
</tr>
<tr>
<td>3</td>
<td>Bayardelle 1954</td>
<td>Suspension</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Mossop 1955</td>
<td>Cloud chamber</td>
<td>± 0.2 K</td>
<td>mercury and silicone</td>
</tr>
<tr>
<td>5</td>
<td>Jacobi 1955</td>
<td>Cold stage</td>
<td>± 0.2 K</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Carte 1956</td>
<td>Cold stage</td>
<td>± 0.6 K</td>
<td>silicone oil</td>
</tr>
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<td>Langham &amp; Mason 1958</td>
<td>Cloud chamber</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Hoffer 1961</td>
<td>Cloud chamber</td>
<td>± 0.5 K</td>
<td>droplets in silicone oil</td>
</tr>
<tr>
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<td>Emulsion</td>
<td>± 0.1 K</td>
<td>water and oil; significant variation from run to run</td>
</tr>
<tr>
<td>11</td>
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<td>DSC</td>
<td>-</td>
<td></td>
</tr>
<tr>
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<td>Broto &amp; Clausse 1976</td>
<td>DSC</td>
<td>± 0.5 K</td>
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</tr>
<tr>
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<td>Broto et al. 1979</td>
<td>DSC</td>
<td>± 0.5 K</td>
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<td>-</td>
<td>very fast droplet growth → droplet size, T from droplet growth model</td>
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<td>Emulsion</td>
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<tr>
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<td>Cloud chamber</td>
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<td></td>
</tr>
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<td>&lt; ± 0.6 K</td>
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<td>28,29</td>
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<td>30(a) 800 nm droplets 31(b) 200 nm</td>
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<td>Cloud chamber</td>
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<td>EDB</td>
<td>± 0.1 K</td>
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<td>Manka et al. 2012</td>
<td>Vibration spectroscopy</td>
<td>-</td>
<td></td>
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<td>TIP4P</td>
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<td>simulation results</td>
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<td>(35)</td>
<td>Sanz et al. 2013</td>
<td>TIP4P/Ice</td>
<td>-</td>
<td>simulation results</td>
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Table 3.4: Dataset of measurements of the homogeneous freezing rate $J_{hom}$ (sorted chronologically: 1952-2013); DSC stands for Differential Scanning Caliometry, EDB for levitated drops in ElectroDynamic Balance.
3.5 Constraining $\sigma_{iw}$ and $\Delta g^\#$ with $J_{hom}$

![Figure 3.10: Homogeneous freezing measured by several authors. A list of all datasets taken into account including the measurement method and the temperature uncertainty can be found in Table 3.4 (horizontal error bars were omitted on account of clarity). Blue colors characterize measurements done before the year 2000, red colors characterize measurements done after the year 2000. The symbols indicate the measurement method: open circled points (◦) Cloud and aerosol chamber experiments (droplet in air); plus signs (+) Cold stage experiments (droplet on a solid plate); open squares (☐) Suspension, emulsion and dispersion experiments (droplet in liquid); open diamonds (◇) Levitated drop in electrodynamic balance; stars (∗) Electron diffraction.](image)

To estimate the nucleation rate $J_{hom}(T)$ the dataset was fitted following a CNT formulation equivalent to Eq. (3.13). A constant prefactor $C_{prefac}$ of $10^{41}$ m$^{-3}$s$^{-1}$, a constant activation energy $\Delta g^\#$, and a linear T-dependent $\sigma_{iw}$ with the reference value $\sigma_{iw,0}$ of [Hardy (1977)] was used:

$$J_{hom} = C_{prefac} \cdot \exp \left( \frac{\Delta g^\#}{k_B T} \right) \cdot \exp \left( - \frac{16\pi \cdot v_{sc}^2 \cdot (29.1 \cdot 10^{-3} + d\sigma_{iw}/dT \cdot T_c^3)}{3(k_B T)^3 \ln(S_i)^2} \right).$$ (3.18)

The fit parameters are thus the slope of $\sigma_{iw}(T)$ ($d\sigma_{iw}/dT$, fit parameter A) and $\Delta g^\#$ (fit parameter B).
In a first step, the fit was done by combining all measurements into one large dataset to investigate the general behavior of the fitting formula. It can be seen in Fig. 3.12 that a reasonable good fit was possible. However, the fitted $\Delta g^\#$ is negative, which translates into a missing activation energy barrier for the nucleation process and therefore does not seem to be reasonable. As the fit is biased by the number of data in each dataset, a weighting function for each measurement value, which is the reciprocal of the number of data in the corresponding dataset, was next introduced giving all datasets equal weight. This may introduce problems, as the quality of each dataset is different. However, not enough information is available to decide which dataset should or should not be taken into account. A physically-meaningful weighting would be the temperature uncertainty of the measurement, as this strongly affects the results (Riechers et al., 2013). Unfortunately this information was not available for quite a few datasets.

Looking at the whole spectrum of measurements in Fig. 3.10 differences in the slope of the data between datasets can be seen. To take such differences into account, a grouped-data object was created out of the individual datasets. With this method, information about the grouping of the data is not lost. The grouping factor is the measurement method and the time of publication. This procedure splits the dataset into several datasets which are fitted separately. An advantage of this method is that the resulting fit parameters of the individual fits can be compared to check...
3.5 Constraining $\sigma_{iw}$ and $\Delta g^\#$ with $J_{\text{hom}}$

<table>
<thead>
<tr>
<th>Fitting method</th>
<th>Fit parameter</th>
<th>Standard deviation</th>
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<tr>
<td>Fit 1</td>
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<td>5.155</td>
</tr>
<tr>
<td></td>
<td>$B = -5.062232$</td>
<td>0.545589</td>
</tr>
<tr>
<td>Fit 2; weighted dataset</td>
<td>$A = 0.130857$</td>
<td>9.023</td>
</tr>
<tr>
<td></td>
<td>$B = 2.591893$</td>
<td>0.746252</td>
</tr>
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<td>Fit 3; mixed-effect model</td>
<td>$A = 0.1240907$</td>
<td>3.925824</td>
</tr>
<tr>
<td></td>
<td>$B = 2.591893$</td>
<td>fixed</td>
</tr>
</tbody>
</table>

Table 3.5: Results of fitting measurement dataset of $J_{\text{hom}}$. $A = d\sigma_{iw}/dT$ in $10^{-3}$ $J$ m$^{-2}$ K$^{-1}$, $B = \Delta g^\#$ in $10^{-20}$ J.

whether the parameters vary among individual datasets. The correlation between the two fit parameters can also be tested. A disadvantage of this method is that small datasets (containing less than three values) have to be excluded. Therefore, the dataset of Broto et al. (1979) and Broto and Clausse (1976) are combined to one dataset, as well as the dataset of Huang and Bartell (1995) and Bartell and Chushak (2003). The datasets of Knopf et al. (2011), Duft and Leisner (2004), Rzesanke et al. (2012), Bayardelle (1954) and Schaefer (1952) were omitted because they are too small and could not be reasonably combined with other datasets.

To take into account the individual characteristics of each dataset, we estimate fixed and random effects for the grouped-data object using a non-linear mixed-effect model (Lindstrom and Bates, 1990, Pinheiro and Bates, 2004). The fixed effects represent the value of the fit parameter throughout all datasets and the random effects the variation in the fit parameter between the individual datasets. The amount of random effects needed can be estimated from the intervals of the fit parameters for the individual datasets resulting from the fit of the grouped data object. Figure 3.13 shows the intervals of the fit parameters for all datasets. The results are sorted by $J$-values (starting with highest nucleation rates). No trend is seen with time (origin of dataset) and/or measurement method.

The fitted parameters differed from dataset to dataset but were correlated (Fig. 3.14). This correlation underlines the earlier statement that the choice of one free parameter influences the other one. Note that because of this correlation, uncertainties of one quantity can be compensated by the other one.

A simplified mixed-effect model was created based on these results. Only the slope of $\sigma_{iw}$ was taken as a fit parameter, having fixed and random effects, while $\Delta g^\#$ obtained from the fit of the weighted dataset was used. The results of the different fitting methods can be found in Table 3.5 and seen in Fig. 3.15. This mixed-effect model, which is statistically the best solution, was used for the further analysis.

Note that using a trustful reference dataset for $J_{\text{hom}}(T)$ instead of using the whole comprehensive dataset from all peer-reviewed articles could improve the analysis (see section 3.6).
Figure 3.12: Statistics of the fitting formula [Eq. (3.18)] for fitting the collected dataset of homogeneous freezing data (see orange curve in Fig. 3.15). Figure (a) shows the standardized residuals plotted against the values of $\ln(J)$. Figure (b) shows the normal q-q plot of the standardized residuals, where the quantiles of the standardized residuals are plotted against the theoretical quantiles from a normal distribution.
3.5 Constraining $\sigma_{iw}$ and $\Delta g^\#$ with $J_{\text{hom}}$

![Graph](image)

Figure 3.13: Results of the fitting parameters A and B from fitting the grouped data object of $J_{\text{hom}}$, sorted by J-values (starting with highest nucleation rates). Each line (y-axis) stands for one dataset labeled by the corresponding number (see Table 4) with the fitting parameter on the x-axis.

![Graph](image)

Figure 3.14: Correlation of the two fitting parameters A and B. The fitting parameter B (y-axis) is plotted against the fitting parameter A (x-axis).
Figure 3.15: Fitting results for $J_{\text{hom}}(T)$ from (a) 190 K - 240 K and (b) 190 K - 260 K compared to the collected homogeneous freezing dataset.
3.5 Constraining $\sigma_{iw}$ and $\Delta g^\#$ with $J_{hom}$

3.5.2 Constraining $\sigma_{iw}$ and $\Delta g^\#$ using the fit of $J_{hom}(T)$

The final fit to $J_{hom}$ (mixed-effect model) obtained in section [3.5.1] gives a picture of the nucleation rate over a wide temperature range. Moreover, the fitted $J_{hom}(T)$ can be used to better constrain the values of $\sigma_{iw}$ and $\Delta g^\#$ found in literature. In the discussion that follows, the fitted $J_{hom}(T)$ was used 1.) to constrain a reasonable range and behavior of $\sigma_{iw}$ and $\Delta g^\#$, and 2.) to evaluate different literature formulations of $\Delta g^\#$ and $\sigma_{iw}$.

1. **Constraints on $\sigma_{iw}$ and $\Delta g^\#$ from $J_{hom}(T)$**

If $J_{hom}(T)$ and $C_{prefac}$ is known, according to Eq. (3.13), one of $\sigma_{iw}$ or $\Delta g^\#$ can be evaluated based on the other. For example, the fitted $J_{hom}(T)$ can be used to predict $\sigma_{iw}$ using different literature formulations for $\Delta g^\#$ (some of which are independent of $\sigma_{iw}$ with the exception of the constant approach from Chen et al. (2008) and the approach with the opposite temperature dependence from Khvorostyanov and Curry (2000)). The results may be evaluated in terms of their temperature dependence and plausibility.

Figure 3.16 shows the fitted nucleation rate $J_{hom}(T)$ for different temperatures (colored lines) as a function of the two parameters $\Delta g^\#$ and $\sigma_{iw}$. The black symbols represent different estimates for $\Delta g^\#$ (a) or $\sigma_{iw}$ (b) as proposed by various authors. These estimates are all independent of $\sigma_{iw}$ (a) or $\Delta g^\#$ (b). For each estimated $\Delta g^\#$ or $\sigma_{iw}$, $\sigma_{iw}$ or $\Delta g^\#$ is constrained by $J_{hom}(T)$ as following a different functional form, as shown by the black lines in Fig. 3.16.

A linear dependence of $\sigma_{iw}$ on temperature (as expected; Section 3.3.1) implies that the black lines in Fig. 3.16(a) should be curved, which can also be seen in Fig. 3.16(b). Where this is not the case, $\sigma_{iw}$ is only linear for low temperatures at low $\Delta g^\#$ where the isolines of $J_{hom}(T)$ are nearly equidistant. Other formulations of $\Delta g^\#$, which lead to a non-linear temperature dependence of $\sigma_{iw}$ [e.g. the one of Chen et al. (2008)], may be interpreted as being inconsistent with theoretical expectations.

The temperature trend in $\sigma_{iw}$ given by the formulation of Pruppacher and Klett (2000) suggests that $\sigma_{iw}$ becomes negative at temperatures below 223 K, which reflects a transition to unstable conditions, where no thermodynamic equilibrium exists. The temperature dependence of $\Delta g^\#(T)$ would need to reverse below this temperature, if $\sigma_{iw}$ is to decrease with $T$ but has a positive value. On the other hand, the $\Delta g^\#$ formulation of Jeffrey and Austin (1997) leads to reasonable values of $\sigma_{iw}$ over the whole temperature range.
Figure 3.16: Plausible combinations of $\sigma_{iw}$ and $\Delta g^\#$ reproducing $J_{hom}$ in the temperature range from 203 K - 258 K (colored lines). (a) Different literature estimates of $\Delta g^\#$ together with the matching $\sigma_{iw}$ are shown in black. The reverse calculation of Reinhardt and Doye (2013) is shown in red meaning the matching $\Delta g^\#$ for their estimate of $\sigma_{iw}$. (b) Different literature estimates of $\sigma_{iw}$ together with the matching $\Delta g^\#$ are shown.
3.5 Constraining $\sigma_{iw}$ and $\Delta g^\#$ with $J_{\text{hom}}$

As shown by the steepness of the $J_{\text{hom}}$ curves in Fig. 3.16 for temperatures above 233 K, $\sigma_{iw}$ is not strongly influenced by the temperature dependence of $\Delta g^\#$. For these temperatures, $\Delta g^\#$ could therefore be approximated as a temperature-independent constant. In contrast, the value of $\Delta g^\#$ becomes increasingly important for lower temperatures. As the size of an ice germ decreases with temperature, it is possible that the capillary assumption (Section 3.1.1) may not hold at these low temperatures.

2. Evaluation of different formulations of $\sigma_{iw}$ and $\Delta g^\#$

Different formulations of $\Delta g^\#$ and $\sigma_{iw}$ were collected from literature and evaluated against the fitted $J_{\text{hom}}(T)$. The selected formulas are independent of one another (the formulations based on theoretical concepts were chosen) with the exception of the Chen et al. (2008) formulation of $\Delta g^\#$, which has been included to see how a temperature independent formulation of $\Delta g^\#$ behaves. Nucleation rates $J_{\text{hom}}(T)$ were calculated using these formulations [Eq. (3.13)] and the difference between these calculated rates and the fitted $J_{\text{hom}}(T)$ was evaluated for the atmospherically-relevant temperature range 230-250 K based on the relative uncertainty at 223 K, 233 K, 243 K and 253 K (Fig. 3.17).

We find that the formulation of $\Delta g^\#$ is of secondary importance between 230 and 250 K. Moreover, while some formulations show good agreement with the fit until 245 K, very few formulations also show good agreement at lower temperatures. The combination of the $\sigma_{iw}$ formulation of Reinhardt and Doye (2013), which is based on molecular model simulations, and the $\Delta g^\#$ formulation of Zobrist et al. (2007), which is based on self-diffusivity measurements, leads to the best agreement with our $J_{\text{hom}}(T)$. The resulting curve is shown with the fit and the homogeneous dataset in Fig. 3.17. Besides in Fig. 3.16(a) it can be seen that both curves lie on top of each other or at least close in this temperature range. However, for low temperatures the combination of both parameters does not give a nucleation rate close to the fitting result (the curves in Fig. 3.16(a) deviate from each other).

Note that this result is self-consistent but has to be used with caution since it is dependent on $J_{\text{hom}}(T)$ and the formulations of $\sigma_{iw}$ and $\Delta g^\#$ used in the analysis.
3 CNT for homogeneous freezing

Due to a poor understanding of the physics of supercooled water, the theory of CNT is poorly constrained. Key thermodynamic and kinetic parameters in the theory remain to be understood. Multiple studies have attempted to define these parameters, using different methods which have resulted in diverse findings. Consequently, multiple different formulations of CNT exist. Depending on the formulation used, CNT-predicted ice nucleation rates may differ widely. This difference contributes significantly to uncertainties in regional and global climate models when CNT-based freezing parameterizations are used.

This study gives an overview of the different thermodynamic and kinetic parameters in CNT. The physical considerations or assumptions which these parameters are based on are summarized, and the uncertainties associated with the choice of their different formulations are discussed. It is concluded that CNT is most sensitive to the interfacial tension between ice and water, \( \sigma_{iw} \). Uncertainties in \( \sigma_{iw} \) dominate uncertainties in the nucleation rate \( J_{\text{hom}} \). While measurements of \( J_{\text{hom}} \) differ by six orders of magnitude at 230 K, predicted values of \( J_{\text{hom}} \) can differ by 25

Figure 3.17: Comparison of the fitted \( J_{\text{hom}}(T) \) (solid black line) with calculated nucleation rates using different formulations of \( \sigma_{iw} \) and \( \Delta g^w \). All lines besides the fitted \( J_{\text{hom}}(T) \) (solid black line) and the best-fitting combination of \( \sigma_{iw} \) and \( \Delta g^w \) (solid blue line) are made transparent to increase clarity.

3.6 Conclusions and outlook
orders of magnitude for the different formulations of $\sigma_{iw}$ in the literature. To reconcile these differences, $\sigma_{iw}$ needs to be known to within approximately 10% accuracy.

To better constrain the two most important free parameters of CNT, $\sigma_{iw}$ and $\Delta g^\#$, we fitted measured homogeneous nucleation rates from 33 droplet freezing experiments which used a variety of experimental techniques. Based on the resulting function $J_{\text{hom}}(T)$ and on literature formulations for the activation energy $\Delta g^\#$, respectively $\sigma_{iw}$, we calculated $\sigma_{iw}$, respectively $\Delta g^\#$, and compared it with literature results. From this analysis it emerged that either $\sigma_{iw}$ is thermodynamically undefined at low ($\approx < 230$ K) temperatures, or the temperature dependence of $\Delta g^\#$ reverses at these temperatures. Further studies are needed to evaluate these possibilities. However, for atmospheric applications, these issues arise outside of the relevant temperature range (but might be important for other fields). Thus it can be concluded that $\Delta g^\#$ can be set to a temperature-independent constant to simplify CNT formulations of atmospheric homogeneous freezing.

Different literature formulations of $\sigma_{iw}$ and $\Delta g^\#$ were also evaluated for consistency with the fitted $J_{\text{hom}}$ in the temperature range $230$ K $< T < 250$ K. It was found that the $\sigma_{iw}$ formulation of Reinhardt and Doye (2013) in combination with the $\Delta g^\#$ formulation of Zobrist et al. (2007) performed best within the framework of this analysis.

Four major issues with regard to constraining CNT remain. First, better measurements or estimates of $\sigma_{iw}$ at the melting point would better constrain $\sigma_{iw}(T)$ for supercooled water. Modern experimental techniques or molecular modeling may be helpful. Second, the behavior and definition of $\sigma_{iw}$ at low temperatures and third, the behavior of $\Delta g^\#$ at these temperatures remains poorly understood. The fourth issue is the nucleation rate itself- reducing the spread in nucleation rate measurements and thus decreasing uncertainty helps to better constrain the free parameters of CNT. This could be done by agreed guidelines for the definition of the experimental parameters and improved experimental control and awareness of uncertainties of $T$, $V_{\text{drop}}$, and $t$. Using such guidelines enables a re-evaluation of the homogeneous freezing datasets to create a trustful reference dataset for $J_{\text{hom}}(T)$.

Note that, because CNT is not a fully constrained theory yet, it would be helpful to specify which formulation and estimates of the free parameters are used when applying CNT to predict nucleation rates or interpret data.

**Remarks and typographical errors found in the literature.** The review of the kinetic and thermodynamic parameters is necessary incomplete due to the large amount of literature on this subject.

One typographical error was found in Pruppacher and Klett (2000): On page 206 $n_s$ (here $N_c$) has to be $5.85 \cdot 10^{14}$ cm$^{-2}$ and $5.3 \cdot 10^{14}$ cm$^{-2}$ instead of
5.85·10^{12} \text{ cm}^{-2} \text{ and } 5.3·10^{12} \text{ cm}^{-2}.

In Taborek (1985) \( \sigma_{iw,0} \) is different from the value given in Table 3.3. The value was calculated using the linear slope \( d\sigma_{iw}/dT \) and the measured value of \( \sigma_{iw} \) at 236 K and deviates most probably from the original value because \( d\sigma_{iw}/dT \) is rounded in the paper to 0.1 J m^{-2} K^{-1}.

Extrapolating the data of Gránásy et al. (2002) is giving a value of 28.6·10^{-3} J m^{-2} for \( \sigma_{iw,0} \) instead of the extrapolated value in the paper (27.1·10^{-3} J m^{-2} \pm 0.2·10^{-3} J m^{-2}).

The equation for the activation energy \( \Delta g^{\#} \) of Khvorostyanov and Curry (2000) stated in Ervens and Feingold (2012) is wrong. The unit has to be erg instead of J (or a conversion factor has to be added) and it is 0.027 instead of 0.0027.

Acknowledgments. The authors would like to thank Joel Corbin for discussions and proof-reading, Matteo Tanadini (Tana) and Sarah Grimm for statistical consulting, Thea Schmitt for discussions about homogeneous freezing datasets, Aleksandra Borodina for the help with the Russian literature and the anonymous reviewers for their input and discussion.
3.A Methods for estimating $\Delta g^\#$

- **Dufour and Defay (1963):**

  In [Dufour and Defay](1963) $\Delta g^\#$ is calculated by using the viscosity of water $\eta$ [see Eq. (3.14)] leading to:

  \[
  \Delta g^\# \text{[J]} = k_B \cdot T \cdot \ln \left( \frac{v_{H_2O} \cdot \eta}{h \cdot N_A} \right). \tag{3.19}
  \]

  For Fig. 3.1 the formulation of [Huber et al. (2009)] is used to calculate the viscosity of water $\eta$ (originally $\eta$ was based on [Dorsey (1940)]).

- **Eadie (1971):**

  Unlike in other publications, the activation energy is estimated based on the dielectric relaxation time of water ($\tau$). For this purpose the measurement of [Collie et al. (1948)] is used and interpolated with a four-point Newton interpolation, which leads to similar results as in [Dufour and Defay (1963)]. An advantage of this method can be seen in Eq. (3.16)- different from the other methods there is no offset value ($\tau_0$) which has to be estimated first.

- **Young (1993):**

  In [Young (1993)] $\Delta g^\#$ is defined as the energy needed to break one hydrogen bond. This energy is estimated based on measurements of the viscosity of supercooled water using a capillary flow technique by [Hallett (1963)] and on measurements of the nucleation process in a cloud chamber at 233.15 K by [Hagen et al. (1981)] leading to:

  \[
  \Delta g^\# \text{[J]} = 3.6 \cdot 10^{-20} - 7.3 \cdot 10^{-22} \cdot T_c \tag{3.20}
  \]

  with $T_c$ the temperature in °C. This formulation is also used by [Chukin et al. (2010)].

- **Pruppacher and Klett (2000):**

  In [Pruppacher and Klett (2000)] $\Delta g^\#$ is estimated from a fit to laboratory data of the self-diffusion coefficient of water. For this the following measurements were used: in the temperature range between 273.15 K and 318.15 K the data based on a diaphragm-cell technique by [Mills (1973)] and the evaluation of [Mills (1971)], where existing measurement data has been listed and reviewed. In the temperature range of supercooled water the data of [Gillen et al. (1972)] and [Pruppacher (1972)] were used. [Gillen et al. (1972)] used a fixed gradient spin-echo nuclear magnetic resonance (NMR) method to measure the self-
diffusivity between 298.15 K and 242.15 K. Pruppacher (1972) did measurements of the self-diffusivity of water in the temperature range of 303.15 K to 248 K. To estimate $\Delta g^\#$ from self-diffusivity measurements an effective activation energy was defined:

$$\Delta g^\# = -R \cdot d(\ln D)/d(T^{-1}) , \quad (3.21)$$

resulting in the following cubic fit of the activation energy:

$$\Delta g^\# [J] = a_0 \cdot \exp(a_1 T_c + a_2 T_c^2 + a_3 T_c^3) , \quad (3.22)$$

with $a_0 = 5.55 \cdot 4184/(6.022 \cdot 10^{23})$ J, $a_1 = -8.423 \cdot 10^{-3}$, $a_2 = 6.384 \cdot 10^{-4}$ and $a_3 = 7.891 \cdot 10^{-6}$, which is valid in the temperature range from 310.15 to 233.15 K [Pruppacher and Klett (2000); Eq. (3.22)].

The method has the disadvantage of implicitly assuming that the temperature dependence of $\Delta g^\#$ is weak compared to the $1/T$-dependence of the exponential in Eq. (3.15), which may not be true for supercooled water (Jeffery and Austin 1997).

- Jeffery and Austin (1997):

Jeffery and Austin used measurements of the self-diffusion of water from Priemeier et al. (1987) and Harris and Woolf (1980) to estimate $\Delta g^\#$. The data from Priemeier et al. (1987) was used to fit the temperature dependence with the Vogel-Fulcher-Tammann (VFT) approach. $D_0$ was estimated from the data of Harris and Wolf, resulting in:

$$\Delta g^\# [J] = \frac{RT}{N_A} \cdot \left( \frac{B}{T - T^*} - \ln \left( \frac{D^*}{D_0} \right) \right) \quad (3.23)$$

with $B = 347$ K$^{-1}$, $T^* = 177$ K, $D^* = 4.14 \cdot 10^{10}$ m$^2$s$^{-1}$ and $D_0 = 349 \cdot 10^{10}$ m$^2$s$^{-1}$.


Khvorostyanov and Sassen discuss an extension to the Pruppacher and Klett (2000) formulation. $\Delta g^\#$ for low temperatures ($T < 243.15$ K) is described as the activation energy across the liquid-ice boundary taking into account enhanced cooperation of molecules when transferring into the ice lattice at low temperatures. Therefore, the sign of $d\Delta g^\#/dT$ is different to all other formulations giving a negative temperature depended relation ($\Delta g^\#$ is decreasing with decreasing $T$). The parameterization is based on fitted values for homogeneous freezing at $T < 243.15$ K following Jensen et al. (1994). Fitting the nucleation
rate with the Pruppacher and Klett (2000) formulation of $\sigma_{\text{iw}}$ results in an activation energy of the following form:

$$
\Delta g^#(J) = 0.694 \cdot 10^{-19} \cdot (1 + 0.027 \cdot (T_c + 30))
$$

Because this equation can give negative values, it was corrected in Khvorostyanov and Curry to

$$
\Delta g^#(J) = 0.694 \cdot 10^{-19} \cdot [1 + 0.027 \cdot (T_c + 30) \cdot \exp(0.01 \cdot (T_c + 30))] 
$$

However, above 243.15 K the Pruppacher and Klett (2000) formulation is used. Note that in this study the label $\Delta g^#$ of Khvorostyanov and Curry (2000) refers only to the extension of the formulation of Khvorostyanov and Curry (2000) (the part of the formulation similar to Pruppacher and Klett (2000) is not shown due to clarity).

- **Zobrist et al. (2007):**

  In Zobrist et al. (2007) an empirical temperature dependent formulation of $\Delta g^#$ is estimated based on measurements of the self-diffusivity by Smith and Kay (1999) in the following form:

  $$
  \Delta g^#(J) = \frac{k_B T^2 E}{(T - T^*)^2}
  $$

  with parameters $E = 892$ K and $T^* = 118$ K. This parameterization is valid in the temperature range of 150 K to 273 K.

  The dataset of the self-diffusivity consists of data between 150 and 157 K and between 250 K and 500 K. The complete dataset cannot be fitted by an Arrhenius temperature dependence, because of a much stronger temperature dependence in the cold range. Other methods to fit the temperature dependence are the often used VFT equation and a power-law ansatz. While the VFT equation is able to fit both temperature ranges, the power law fails to fit the cold range like the Arrhenius fit. However, the power law better represents the data above 250 K, thus the ideal method depends on the temperature regime of interest. Zobrist et al. (2007) used the VFT equation to describe $\Delta g^#$.

- **Chen et al. (2008):**

  In Chen et al. (2008), $\Delta g^#$ is used as a fit parameter in CNT. The parameter was estimated for immersion freezing assuming that it is temperature independent over the temperature range of this freezing process (approximately 238.15 to 273.15 K). Because the diffusion of a molecule across phases should not be influenced by the presence of insoluble substances in the water droplet, $\Delta g^#$ should be the same for heterogeneous and homoge-
neous freezing. Moreover it should also be independent of the aerosol type (in case of heterogeneous freezing). However, because it was used as a fit parameter, it varies from dataset to dataset and thus for different aerosol types in this study. The value of $\Delta g^\#$ varies from $12.7 \cdot 10^{-20}$ J (soot) to $16 \cdot 10^{-20}$ J (China rose pollen). A value in-between of $14.5 \cdot 10^{-20}$ J is used here as shown in Fig. 3.1. Besides, the result from the fitting method used depends on the estimate of other free parameters, most important on $\sigma_{iw}$. 
3.B Methods for estimating $n_s$

The number of water molecules in contact with the unit area of the ice germ $n_s$ is a surface dependent factor, which is estimated by different authors:

- **Fletcher (1962):**

  The number of molecules in contact with the unit area of an ice germ or a catalyst surface (as in the case of immersion freezing) can be estimated from the molecular density of water $N_l$:

  \[ n_s \text{[m}^{-2}\text{]} = 3 \cdot 10^{-10} \cdot N_l \, . \quad (3.26) \]

  The factor $3 \cdot 10^{-10}$ represents the side dimension of a cube containing one mole of water (approx. $3 \cdot 10^{-29} \text{ m}^3 \text{ mol}^{-1}$). At 273.15 K $n_s$ is approximately $10^{19} \text{ m}^{-2}$.

  The same approximation is used by Young (1993) and Khvorostyanov and Curry (2004). Zobrist et al. (2007) and Chen et al. (2008) assume that $n_s$ is independent on temperature and use the value at 273.15 K ($10^{19} \text{ m}^{-2}$) for the whole temperature range.

- **Dufour and Defay (1963):**

  In Dufour and Defay (1963) $n_s$ is calculated for a spherical germ by:

  \[ n_s \text{[m}^{-2}\text{]} = \alpha \cdot r_{\text{germ}}^{2/3} \, , \quad (3.27) \]

  where $\alpha$ is a constant. To estimate $n_s$, Dufour and Defay (1963) calculated the distance of two neighboring water molecules in tetrahedral arrangement and came up with 2.69 Å at 277.15 K. For that distance they approximated a value for $n_s$ of $5.21 \cdot 10^{18} \text{ m}^{-2}$ in the planes (100)(010)(001). In the planes (110)(101)(011) it is $7.4 \cdot 10^{18} \text{ m}^{-2}$. For their calculations they used a value of $5.3 \cdot 10^{18} \text{ m}^{-2}$. They show, that the higher value of $7.4 \cdot 10^{18} \text{ m}^{-2}$ changes the nucleation rate by a factor of 1.4. It has a minor effect on the freezing temperature (0.1 K to 0.3 K for small droplets).

  In Pruppacher and Klett (2000) as well as Jeffery and Austin (1997) (referring to Pruppacher and Klett (2000)) a value within the above mentioned range of $5.85 \cdot 10^{18} \text{ m}^{-2}$ is used.
Due to the fact that $\sigma_{iw,0}$ can only be measured indirectly several measured data exist, which are explained below:

- **Kubelka and Prokscha (1944):**

  Kubelka and Prokscha used several capillary methods to estimate $\sigma_{iw}$ from the melting point reduction in the pores of a silica gel using the Thomson equation at approximately 268.15 K. They found an averaged value of $25.4 \cdot 10^{-3}$ J m$^{-2}$, a minimum value of $21.9 \cdot 10^{-3}$ J m$^{-2}$ and a maximum value of $27.9 \cdot 10^{-3}$ J m$^{-2}$.

- **Skapski et al. (1957):**

  Skapski et al. (1957) used a Pyrex tube as a capillary cone in which they measured the ice-water equilibrated interface curvature with a microscope. From the deviation of the melting temperature from 273.15 K they estimated the interfacial tension using the Gibbs-Thomson relation resulting in a rather high value for $\sigma_{iw,0}$ of $44 \cdot 10^{-3} \pm 10 \cdot 10^{-3}$ J m$^{-2}$. This might be due to inaccurate measurements of the curvature or impurities inside the cone, which might lower the melting point (Hardy, 1977).

- **Fernandez and Barduhn (1967):**

  Fernandez and Barduhn (1967) measured the crystal growth of ice crystals in supercooled water with different flow velocities. They found an interfacial tension of $31.8 \cdot 10^{-3} \pm 1.8 \cdot 10^{-3}$ J m$^{-2}$.

- **Coriell et al. (1971):**

  Coriell et al. (1971) observed the growth of ice crystal cylinders into supercooled water. The measured growth rates and wavelength of sinusoidal perturbations were then used to estimate $\sigma_{iw,0}$ of $25 \cdot 10^{-3}$ J m$^{-2}$.

- **Ketcham and Hobbs (1969):**

  In Ketcham and Hobbs (1969) the equilibrium conditions of grain boundary grooves at the liquid-solid interface were investigated and the shape of the grain boundary grooves (grain boundary groove angle) measured. The Young relation (Young, 1805) was then used to estimate $\sigma_{iw,0}$ from the contact angle leading to $33 \cdot 10^{-3} \pm 3 \cdot 10^{-3}$ J m$^{-2}$.

- **Jones and Chadwick (1970):**
3.C Methods for estimating $\sigma_{iw}$ at the melting point ($\sigma_{iw,0}$)

Jones and Chadwick [1970] also used grain boundary measurements, but found a quite different value of $\sigma_{iw,0}$ of $41 \cdot 10^{-3} \pm 9 \cdot 10^{-3}$ J m$^{-2}$. The measurement was therefore redone by Jones [1974] leading to a value of $44 \cdot 10^{-3} \pm 10 \cdot 10^{-3}$ J m$^{-2}$. Since the error of this measurement is large, the lower value by Ketcham and Hobbs [1969] is almost entirely inside the uncertainty range of Jones [1974]. The used technique might not work for materials with different thermal conductivities in the liquid and solid phase as in the case of water [Hardy 1977].

- **Hardy [1977]:**

  Similar as in Ketcham and Hobbs [1969] and Jones and Chadwick [1970] the equilibrium shape of grain boundary grooves at a stabilized melt-crystal interface is observed with a slightly different experimental setup compared to Ketcham and Hobbs [1969]. Different from Ketcham and Hobbs [1969], $\sigma_{iw,0}$ is indirectly estimated using the analysis from Nash and Glicksman [1971]. It results in a value of $29.1 \cdot 10^{-3} \pm 0.8 \cdot 10^{-3}$ J m$^{-2}$. The measurement of $\sigma_{iw,0}$ by Hardy [1977] is considered as the most reliable (e.g. Gránásy et al. [2002]).

- **Hillig [1998]:**

  Hillig [1998] used fine-pore cellulose acetate filters with pore sizes corresponding to the minimum gas pressure allowing bubbling through the water-wetted filters. The corresponding supercooling was measured. From the proportionality between the supercooling and the gas pressure the interfacial tension was calculated. The measurement was repeated for different filter types leading to an average value of $\sigma_{iw,0}$ of $31.7 \cdot 10^{-3} \pm 2.7 \cdot 10^{-3}$ J m$^{-2}$.

Additionally to measured values some studies did theoretical calculation to estimate $\sigma_{iw}$. Thus Volmer [1939] suggested to estimate $\sigma_{iw,0}$ based on the assumption that the relation of $\sigma_{iw}$ to the latent heat of melting $L_m$ is equivalent to the relation of $\sigma_{wa}$ to the latent heat of vaporization $L_v$. The approach was used by Krastanow [1941]. However, assuming $L_v$ to be constant did result in a wrong temperature behavior of $\sigma_{iw}$. The calculated values of Krastanow [1941] were later corrected by McDonald [1953] using a temperature dependent $L_v$ parameterization. Only the corrected values are plotted in Fig. 3.2. Turnbull [1950] used a similar approach and did relate $\sigma_{iw}$ to the heat of melting per unit area and thus estimated $\sigma_{iw,0}$ for different materials including water.

Moreover Oura [1950] estimated $\sigma_{iw}$ from nucleation measurements of Schaefer [1952] and Smith-Johannsen [1948] by using the formulation of Turnbull and Fisher [1949]. He found a value of $18.5 \cdot 10^{-3}$ J m$^{-2}$ at 253.15 K by theoretical considerations.
Another approach was suggested by Born and Stern (1919). It is based on the lattice energy of the ice crystal (cleavage work), which is computed from the energy of hydrogen bonds and Antonoff's rule (Antonoff, 1939). Using this method Mason (1952) estimated a value for $\sigma_{iw}$ of $22 \cdot 10^{-3}$ J m$^{-2}$ at 233.15 K. Briegleb (1949) re-estimated the energy of the hydrogen bonds at the surface and thus the interfacial tension $\sigma_{iw}$. McDonald (1953) reviewed the method of Mason and suggested that the energy of hydrogen bonds at the surface calculated from the sublimation heat has to be corrected and the distortion energy has to be taken into account leading to new estimates for the temperature range from 223.15 to 273.15 K. However, the general assumption, specifically the Antonoff's rule (Antonoff, 1939), for the calculation is criticized by Ouchi (1954). Gilra and Dass (1968) followed another theoretical approach by using precrystallization theory. They calculated low values of $13 \cdot 10^{-3}$ J m$^{-2}$ and $10 \cdot 10^{-3}$ J m$^{-2}$ at 263.15 K and 253.15 K, respectively.

Manka et al. (2012) found an interfacial tension of $15.6 \cdot 10^{-3}$ J m$^{-2}$ in the temperature range from 202 to 215 K from nucleation rate measurements using the analysis from Murray et al. (2010).
3.D Methods for estimating $\sigma_{lw}(T)$

The different forms of $\sigma_{lw}(T)$ found in literature stem from the use of either a macroscopic value from the list above in combination with a theoretical temperature dependence, a theoretical approach only, a macroscopic value in combination with nucleation measurements, the use of nucleation measurements only or the use of molecular simulations. The estimates for the interfacial tension are therefore dependent on the chosen macroscopic value, the nucleation rate dataset used for fitting, the theoretical assumption of the temperature dependence or the type of molecular model. Some descriptions of all methods will be compared in the following.

- **Young relation (1805):**

  Young’s semi-empirical relation is based on the mechanical equilibrium conditions of a drop on a solid surface. In this case the interfacial tension between the solid and air ($\sigma_{sa}$) is in balance with the interfacial tension between solid and water ($\sigma_{sw}$) and the one between water and air ($\sigma_{wa}$) multiplied by the cosine of the contact angle $\alpha$ between the drop and the substrate:

  \[ \sigma_{wa} \cdot \cos \alpha = \sigma_{sa} - \sigma_{sw} . \]  

  (3.28)

  For $\alpha$ going towards zero Eq. (3.28) can be used, following Antonoﬀ (1939), to indirectly calculate $\sigma_{lw}$ from $\sigma_{ia}$ and $\sigma_{wa}$ as they are in equilibrium:

  \[ \sigma_{lw} = \sigma_{ia} - \sigma_{wa} . \]  

  (3.29)

  $\sigma_{wa}$ can be found in Pruppacher and Klett (2000). The formulation of Pruppacher and Klett (2000) is taking into account the singularity behavior of water near 228.15 K. $\sigma_{ia}$ is given e.g. in Hale and Plummer (1974).

- **Ouchi (1954):**

  Ouchi (1954) derived the temperature dependence of $\sigma_{lw}$ based on thermodynamics. He assumed that the interface of liquid and ice is a layer of the same amount of ice and water molecules. In this layer the mean internal energy per molecule is

  \[ U = \frac{1}{2} \cdot (2U_w + 2U_i) = \Delta U + 2U_i \]

  with $\Delta U$ being the difference of the internal energy per molecule related to the different phases $U_w - U_i$. 

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Due to mixing of molecules with different phases the entropy is changing. For a large number of molecules ($n$) the entropy ($S$) becomes

$$S = n \cdot k_B \cdot \log(2).$$

As the free energy ($F$) is defined as $F = U - TS$, the interfacial free energy per molecule is equal to $F_{\text{molecule}} = U - k_B \cdot \log(2)$. The interfacial free energy (interfacial tension) per unit area of the interface is thus the following:

$$\sigma_{iw} \left[\text{J m}^{-2}\right] = \frac{U - k_B \cdot \log(2)}{\left(\frac{V_{\text{ice}}}{N_A}\right)^{2/3}}$$  \hspace{1cm} (3.30)

with $V_{\text{ice}}$ is the volume of one gram molecule of ice.

- **Jacobi (1955) and Dufour and Defay (1963):**

  Jacobi (1955) estimated $\sigma_{iw}$ from his own nucleation dataset by using the theory of Volmer (1939) for the phase differences, where $\sigma_{iw}$ is estimated based on the proportion relation of $\sigma_{iw}$ to the latent heat of melting $L_m$ compared to $\sigma_{wa}$ to the latent heat of vaporization $L_v$. Comparison with nucleation measurements lead to a temperature gradient of:

  $$d\sigma_{iw}/dT = 0.2 \cdot 10^{-3} \text{ J m}^{-2} \text{ K}^{-1}$$  \hspace{1cm} (3.31)

  and $\sigma_{iw} = 16.1 \cdot 10^{-3} \text{ J m}^{-2}$ at 238.15 K.

  In Dufour and Defay (1963) $\sigma_{iw}$ was re-estimated from the same dataset using the method of least squares to a regression line for $d\sigma_{iw}/dT$ resulting in:

  $$d\sigma_{iw}/dT = 0.102 \cdot 10^{-3} \text{ J m}^{-2} \text{ K}^{-1}$$  \hspace{1cm} (3.32)

  The value of $\sigma_{iw}$ was estimated to be $20.24 \cdot 10^{-3} \text{ J m}^{-2}$ at 238.15 K.

  This estimate is quite different to the one of Jacobi (1955). The deviation comes mainly from a different formula for the germ radius and a different shape factor (assuming the germ to be a hexagonal prism).

- **Wood and Walton (1970):**

  In this study Wood and Walton measured the kinetics of homogeneous ice nucleation. By fitting CNT to these measurements they derived $\sigma_{yw}$ at 236.6 K and $d\sigma_{yw}/dT = 0.211 \cdot 10^{-3}$
Methods for estimating $\sigma_{iw}(T)$

$\pm 0.012 \cdot 10^{-3} \text{ J m}^{-2} \text{ K}^{-1}$ (in their study denoted as the nucleation parameter $\omega$) resulting in:

$$\sigma_{iw}[\text{J m}^{-2}] = \sigma_{iw,0} + d\sigma_{iw}/dT \cdot T_c \quad (3.33)$$

with $\sigma_{iw,0} = 31.93 \cdot 10^{-3} \pm 0.44 \cdot 10^{-3} \text{ J m}^{-2}$.

- **Eadie (1971)**:

  Eadie gave a full theoretical description of homogeneous nucleation based on a statistical model for liquid water. The basis of the model is the theoretical framework from Némethy and Scheraga (1962), where the specific interfacial tension is a variable of the molecular interactions at the ice-water interface. $\sigma_{iw}$ is obtained as a function of supercooling (see Table 3.6). For a hexagonal plate a value of $23.42 \cdot 10^{-3} \text{ J m}^{-2}$ was determined at a temperature of 238.15 K. The estimate of $\sigma_{iw}$ is limited by the idealized model used.

<table>
<thead>
<tr>
<th>$T_c$ [°C]</th>
<th>Basal face $\sigma_{iw}$ [$10^{-3} \text{ J m}^{-2}$]</th>
<th>Prism face $\sigma_{iw}$ [$10^{-3} \text{ J m}^{-2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>24.4</td>
<td>26.02</td>
</tr>
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</tr>
<tr>
<td>-50</td>
<td>21.67</td>
<td>23.11</td>
</tr>
</tbody>
</table>

Table 3.6: Specific $\sigma_{iw}$ computed by Eadie (1971).

- **DeMott and Rogers (1990)**:

  Nucleation rate measurements were used to estimate $\sigma_{iw}$ from CNT. In the temperature range between 239.15 K and 233.15 K a constant value of $22.5 \cdot 10^{-3} \text{ J m}^{-2}$ was found to best reproduce the data. Extending the range to 243.15 K and taking the temperature dependence into account yields:

  $$\sigma_{iw}[\text{J m}^{-2}] = 28 \cdot 10^{-3} \text{ J m}^{-2} + 0.167 \cdot 10^{-3} \text{ J m}^{-2} \cdot \text{C}^{-1} \cdot T_c \quad (3.34)$$

- **Pruppacher and Klett (2000)**:
Pruppacher and Klett (2000) used an estimate of $\sigma_{iw,0}$ based on unpublished data on latent heat of melting in combination with an educated guess about the temperature dependence. It is expressed by a polynomial expression [Eq. (5-47a) and Eq. (5-47b) in the textbook]:

Between 237.15 and 273.15 K:

$$\sigma_{iw} [\text{J m}^{-2}] = 28 \cdot 10^{-3} \text{J m}^{-2} + 0.25 \cdot 10^{-3} \text{J m}^{-2} \cdot \text{C}^{-1} \cdot T_c \quad (3.35)$$

And between 237.15 and 229.15 K:

$$\sigma_{iw} [\text{J m}^{-2}] = (189.081 \text{J m}^{-2} + 13.1625 \text{J m}^{-2} \cdot \text{C}^{-1} \cdot T_c $$

$$+ 0.3469 \text{J m}^{-2} \cdot \text{C}^{-2} \cdot T_c^2 + 3.125 \cdot 10^{-3} \text{J m}^{-2} \cdot \text{C}^{-4} \cdot T_c^3) \cdot 10^{-3}. \quad (3.36)$$

This formulations are also used by e.g. Chen et al. (2008) and Khvorostyanov and Sassen (1998).

**Jeffery and Austin (1997):**

The interfacial tension $\sigma_{iw}$ in Jeffery and Austin (1997) is calculated empirically by a relation which is based on Turnbull (1950). It is expressed as follows:

$$\sigma_{iw} [\text{J m}^{-2}] = k_T \cdot L_m \cdot \rho_i^{2/3} \cdot N_A^{-1/3} - k_{\sigma} \cdot T, \quad (3.37)$$

where $k_T$ is a constant with a value of 0.32 for water, $L_m$ the latent heat of melting, $\rho_i$ the surface density of ice, $N_A$ the Avogadro constant and $k_{\sigma} = 0.00009 \text{J m}^{-2} \text{K}^{-1}$ another constant estimated by Jeffery and Austin through fitting CNT based nucleation rates to observations. The latent heat of melting is expressed through the change of the specific entropy ($s$) by the equation of state $L_m = T(s_w - s_i)$, where the specific entropy of water ($s_w$) is the inverse change of the specific free energy ($f$) with temperature $s_w = -\left(\frac{\partial f}{\partial T}\right)_{1/p_w}$ and the specific entropy of ice ($s_i$) is $s_i = 1.885 \cdot \log(T) + 0.132 \cdot T - 5.115$, which results from the integration of the heat capacity of ice (Jeffery and Austin, 1997, Pruppacher and Klett 2000).

**Taborek (1985) and Gránásy et al. (2002):**

In Taborek (1985) homogeneous nucleation rate measurements were used to estimate $\sigma_{iw}$ from CNT. The best fit at 236 K resulted in an interfacial tension of $28.3 \cdot 10^{-3} \text{J m}^{-2}$ with a temperature dependence of $d\sigma_{iw}/dT = 0.1 \cdot 10^{-3} \text{J m}^{-2} \text{K}^{-1}$ leading to a value of $31.9 \cdot 10^{-3} \text{J m}^{-2}$ at 273.15 K. $\Delta g^*$ was held constant at $3.4 \cdot 10^6 \text{J}$, which resulted from low-viscosity measurements from Hallett (1963). As the nucleation rate in the investigated temperature range is dominated by the interfacial tension, this simplification causes
3. Methods for estimating $\sigma_{iw}(T)$

only minor uncertainties. However, note that the value is very small compared to other literature estimates (see Appendix 3.A).

Gránásy et al. (2002) used a continuum model instead of the CNT to estimate $\sigma_{iw}$ from nucleation measurements. The approach stems from a generalization of density functional theories and is the single-order-parameter Cahn-Hilliard approach. They reanalyzed the data from Taborek (1985). The interfacial tension at $T = 236$ K was estimated to be approx. $24.8 \cdot 10^{-3}$ J m$^{-2}$, which is slightly lower than the estimate by Taborek (1985). However, they found the same temperature dependence, so that the extrapolated value at $T = 273$ K is $27.1 \cdot 10^{-3} \pm 0.2 \cdot 10^{-3}$ J m$^{-2}$. Gránásy et al. (2002) mention that the crystal in their model analysis could be described with bulk properties in the temperature range of the measurement data.

- **Zobrist et al. (2007):**

$\sigma_{iw}$ is used as a fit parameter in Zobrist et al. (2007). CNT is fitted to experimental nucleation rates from Pruppacher and Klett (2000), Krämer et al. (1999), Duff and Leisner (2004), Benz et al. (2005), Stöckel et al. (2005) and Kabath et al. (2006). For the formulation of the nucleation rate, Eq. (3.13) is used with a kinetic prefactor $Z = 1$ and $N_1 = 3.1 \cdot 10^{28}$ m$^{-3}$ for the volume number density of water molecules in the liquid. The resulting formula for $\sigma_{iw}$ is the following:

$$\sigma_{iw} [\text{J m}^{-2}] = 10^{-2} \text{J m}^{-2} \cdot [3.298 + 1.2048 \cdot \frac{T - T_0}{T_0} - 46.705 \cdot \left(\frac{T - T_0}{T_0}\right)^2].$$

It is valid in the temperature range between 229 and 238 K. However, the extrapolation to 273.15 K yields $32.98 \cdot 10^{-3}$ J m$^{-2}$ and fits to the measured value of Hobbs et al., indicating that the formula can be used over this whole temperature range.

- **Huang and Bartell (1995) and Murray et al. (2010):**

Huang and Bartell proposed that due to lower free energy barrier metastable cubic ice forms first after the phase transition. At homogeneous freezing temperatures it rapidly transforms into the stable hexagonal structure. This assumption is also made by Murray et al. (2010). Both estimate $\sigma_{iw}$ based on their nucleation measurements by fitting the following formula:

$$\sigma_{iw} = \sigma_{iw}(T_{ref}) \cdot \left(\frac{T}{T_{ref}}\right)^n. \quad (3.38)$$

Huang and Bartell (1995) got a result of $n = 0.3$ and $\sigma_{iw}(T_{ref}) = 21.55 \cdot 10^{-3}$ or $21.72 \cdot 10^{-3}$ J m$^{-2}$ at $T_{ref} = 200$ K depending on the used dataset (in Fig. 3.2 the average is used). Murray et al. (2010) report $n = 0.97$ and $\sigma_{iw}(T_{ref}) = 20.8 \cdot 10^{-3} \pm 1.2 \cdot 10^{-3}$ J m$^{-2}$
at $T_{\text{ref}} = 235.8$ K by plotting the logarithm of the measured nucleation rate against $T^{-3} (\ln S_i)^2$ [see Eq. (8) in Murray et al. (2010)]. As the structure of ice is assumed to be cubic here, a direct comparison to other values of $\sigma_{iw}$ for hexagonal ice is difficult. Assuming the structure of the ice to be hexagonal yields $\sigma_{iw}(T_{\text{ref}}) = 26.8 \cdot 10^{-3} \pm 0.5 \cdot 10^{-3}$ J m$^{-2}$.

- **Chukin et al. (2010):**

  Chukin et al. (2010) used a parameterization for $\sigma_{iw}$ based on Pruppacher and Klett (2000) and Berkyae (1991):

  $$\sigma_{iw} [\text{J m}^{-2}] = -0.0397875 \text{ J m}^{-2} + 0.00025 \text{ J m}^{-2} \text{ K}^{-1} \cdot T.$$  

  (3.39)

  It is valid from 233 K to 273 K.

- **Němec (2013):**

  $\sigma_{iw}$ was estimated by fitting nucleation measurement data to CNT in the temperature range of 200-240 K, leading to:

  $$\sigma_{iw} [\text{J m}^{-2}] = \sigma_{iw,0} \cdot \left( \frac{T}{235.8} \right)^n$$  

  (3.40)

  with $\sigma_{iw,0} = 23.24 \cdot 10^{-3} \pm 1.1 \cdot 10^{-3}$ J m$^{-2}$ and the exponent $n = 0.35$. The nucleation measurements, which were used, were the high pressure measurements from Huang and Bartell (1995) and Manka et al. (2012), the dataset from Hagen et al. (1981) and the dataset from Stan et al. (2009). The pressure dependence of the nucleation rate was explicitly described and taken into account.

The use of molecular models to simulate the molecular dynamics and thermodynamics has only recently become feasible. These models are explicitly simulating molecular mechanics of water molecules building clusters. They are classified with respect to the amount of points describing one water molecule i.e. the interaction between water molecules. Depending on the number of points used, the structure and other features, e.g. the polarization of the water molecules, can be represented in the model. One of the simplest models is the TIP4P model of water. It is used in nearly all of the following studies from which the results for $\sigma_{iw}$ are summarized. The abbreviation stands for “4-point-transferable-intermolecular-potential”. The four points refer to both hydrogen atoms, the oxygen atom and the negative charge from the oxygen atom, which is treated separately from the atom and placed near the oxygen at the dipole axis. The angle, shape and body of the water molecule is rigid without any intermolecular forces. Some subversions of the TIP4P model exist, which are the TIP4P-Ew model, using Ewald summation, the TIP4P/Ice model, which is specifically designed for ice, and the TIP4P/2005 model, which
3. D Methods for estimating $\sigma_{iw}(T)$

is capable to simulate the whole phase diagram of condensed water. Results from these models for the estimation of $\sigma_{iw}$ are given in the following. It should be mentioned that the values of $\sigma_{iw}$ can be quite different in the case of a planar calculation of $\sigma_{iw}$ compared to a molecular $\sigma_{iw}$.

- **Digilov** (2004):

  Digilov used Monte Carlo simulations to model the liquid-solid interface and the atomic disordering in the solid-liquid transition zone. From that, the potential function of the interplanar adhesion can be estimated and used to find a relation for $\sigma_{iw}$ based on the empirical Turnbull rule, where $\sigma_{iw}$ is correlated with the melting point temperature ($T_0$) and the latent heat of melting at $T_0$. The relation found scales with $T_0$ and the atomic volume ($\Omega_{sm}^\frac{2}{3}$):

  \[
  \sigma_{iw,0} \approx \frac{3}{2} \cdot \frac{k_B T_0}{\Omega_{sm}^\frac{2}{3}} \cdot \delta^2 \cdot \exp\left(\frac{L_m(T_0)}{3k_B T_0}\right) \quad (3.41)
  \]

  \[
  \approx \frac{1}{8} \cdot \frac{3k_B}{S_m} \cdot \exp\left(\frac{S_m}{3k_B}\right) \cdot \frac{L_m(T_0)}{\Omega_{sm}^\frac{2}{3}} \quad (3.42)
  \]

  where $\delta$ is a displacement factor with a value between 0.5 (lower limit for $\sigma_{iw}$) and 0.7. The second form of the equation is equivalent to the Turnbull rule. It yields a value of $38.7 \cdot 10^{-3}$ J m$^{-2}$ at $T_0$ (Ice hcp).

- **Davidchack et al.** (2012):

  In Davidchack et al. (2012) an extended cleaving method was used, meaning that separate liquid and solid water systems were cleaved and both cleaving potentials were merged to one interface to study the planar interfacial tension. The authors concluded from the simulations that $\sigma_{iw}$ could be due to the short-range packing interaction between water molecules. They did the simulation with the TIP4P, the TIP4P-Ew and the TIP5P-E model setup leading to similar values of $\sigma_{iw,0}$ of $26.5 \cdot 10^{-3}$, $27.6 \cdot 10^{-3}$ and $28.9 \cdot 10^{-3}$ J m$^{-2}$, respectively.

- **Reinhardt and Doye** (2013):

  Reinhardt and Doye used a hybrid Monte Carlo molecular simulation of TIP4P/2005 to estimate $\sigma_{iw}$. At a temperature of 240 K, $\sigma_{iw}$ was found to be approximately $24 \cdot 10^{-3}$ J m$^{-2}$ for monatomic water and $24.5 \cdot 10^{-3}$ J m$^{-2}$ for a basal plane of TIP4P ice. The tempera-
ture dependence of $\sigma_{iw}$ is described by the change in entropy, which occurs per unit area when forming an interface:

$$\left( \frac{\partial \sigma_{iw}}{\partial T} \right)_p = -S.$$ \hspace{1cm} (3.43)

The change of internal entropy $S$ was found to be $0.18 \cdot 10^{-3}$ J m$^{-2}$ K$^{-1}$.

- Sanz et al. (2013):

Sanz et al. (2013) used the TIP4P model to simulate an ice Ih cluster surrounded by supercooled water in the temperature range from 238.15 K to 258.15 K. The information gained about the critical cluster was then combined with CNT to estimate $\sigma_{iw}$ as the size of the critical cluster is strongly correlated with the interfacial tension. The clusters had a size of 600 to 8000 molecules (radius 1.7 to 4 nm), from which the plane in contact with the supercooled liquid and thus $\sigma_{iw}$ was calculated. Sanz et al. (2013) derived a value of $28.7 \cdot 10^{-3}$ J m$^{-2}$ at the melting point and a temperature dependence of $d\sigma_{iw}/dT = 0.18 \cdot 10^{-3}$ J m$^{-2}$ K$^{-1}$.

To counteract the problem that $\sigma_{iw}$ is a macroscopic property and might be different in case of small clusters of water molecules, Bogdan (1997) estimated the curvature effect on $\sigma_{iw}$ following Tolman (1948). As a basis he used the formulation of Dufour and Defay (1963) and the Gibbs (1948) relations. He found that $\sigma_{iw}$ decreases with curvature (resulting in smaller critical clusters), which on the other hand then increases the probability of nucleation.
Sensitivity of immersion freezing to thermodynamic and kinetic parameters and derivation of CNT parameter from laboratory data

There are different possibilities how to describe the properties of aerosol particles (i.e. contact angle schemes) within the framework of CNT, which are compiled and tested in this chapter. The goal of this chapter is to find a parameterization scheme for GCMs to describe immersion freezing with the ability to shift and adjust the slope of the freezing curve compared to homogeneous freezing to match experimental data.

The results of using CNT are very sensitive to unconstrained kinetic and thermodynamic parameters in the case of homogeneous freezing leading to uncertainties in calculated nucleation rates $J_{\text{hom}}$ of several orders of magnitude. Here we investigate how sensitive the outcome of a parameter estimation for contact angle schemes from experimental data is to kinetic and thermodynamic parameters. We show that additional free parameter can mask the uncertainty of $J_{\text{imm}}$ due to thermodynamic and kinetic parameters.

Different CNT formulations are fitted to an extensive immersion freezing dataset as a function of particle diameter ($d$), temperature $T$ and time $t$ for different mineral dust types, namely kaolinite, illite, montmorillonite, microcline (K-feldspar) and Arizona test dust. It is investigated how accurate different CNT formulations (with the estimated fit parameters) reproduce the measured freezing curves, especially the time and particle size dependence of the freezing process. The results are compared to a simplified deterministic freezing scheme. It is evaluated in this context which CNT based parameterization scheme to represent particle properties is a good choice to describe immersion freezing in a GCM.

Introduction

In mixed-phase clouds freezing of cloud droplets occurs by different pathways of heterogeneous freezing/nucleation. The nucleation process is initiated on the surface of an aerosol particle, called ice nucleus (IN), which either collides with a supercooled droplet (contact freezing), acts as cloud condensation nucleus (CCN) and causes freezing when the droplet is increasingly supercooled (immersion freezing), freezes immediately after CCN activation at supercooled conditions (condensation freezing), or provides a site where water vapor deposits as ice (deposition nucleation) (Vali, 1985b).

In mid latitudes, where supercooled clouds are common, IN and their effect on precipitation formation through immersion freezing influence the hydrological cycle (DeMott et al., 2010, Lohmann, 2002, Zeng et al., 2009) and thereby e.g. the biosphere and agriculture. Aerosol particles determine the formation and ice-water ratio of mixed-phase clouds, thereby the cloud radiative properties and indirectly the radiation budget, which affects earth’s climate. Therefore results of climate simulations in regional and global models are sensitive to the parameterization scheme used for heterogeneous ice formation and in particular immersion freezing as it is the most abundant freezing pathway (Ansmann et al., 2009, Wiacek et al., 2010). One approach to parameterize immersion freezing in global and regional climate models is by Classical Nucleation theory (CNT). CNT is a theory based on approximations considering the thermodynamics and kinetics of nucleation. Although computationally more expensive in most cases compared to empirical parameterization schemes, it allows a physical treatment of ice nucleation as function of temperature $T$, ice supersaturation $S_i$, time $t$ and IN type (e.g. size, surface properties).

Using a theoretical scheme has the advantage that the scheme is valid over the whole $T$-$S_i$-space, which is mandatory for the use in a GCM, where all kind of conditions occur (especially in certain regions, but also in simulations of future climate, where atmospheric conditions can be different from the present day or pre-industrial ones). Empirical schemes are in contrast often limited to narrow conditions the scheme was estimated for and can lead to unphysical results when extrapolated. Therefore empirical schemes might not hold for future atmospheric or untypical atmospheric conditions. One example is the Meyers et al. (1992) scheme, which was developed using measurements in mid-latitude and has problems when being extrapolated to Arctic conditions (Prenni et al., 2007).

The framework of CNT is partly unconstrained and therefore very sensitive to the choice of thermodynamic and kinetic parameters, namely interfacial tension between ice and water $\sigma_{iw}$ and activation energy $\Delta g^\#$. Sensitivity of CNT on $\sigma_{iw}$ and $\Delta g^\#$ in the case of homogeneous freezing has been discussed in chapter 3. Using CNT as an approach to parameterize immersion freezing in aerosol-climate models raises the question of the sensitivity of the parameterization scheme to $\sigma_{iw}$ and $\Delta g^\#$ in the case of heterogeneous freezing. Additionally there is a need to include and represent IN properties. Here we use three different schemes to describe the effect...
of an IN population on immersion freezing and investigate the impact of the chosen scheme on the parameterization of immersion freezing. We also discuss strategies how to judge/evaluate different CNT formulations.

The formalism of CNT for immersion freezing is explained in section 4.1. Advantages and disadvantages of certain formulation for the use in GCMs are discussed. In section 4.2 the sensitivity of the immersion freezing nucleation rate \( J_{\text{imm}} \left[ \text{s}^{-1} \text{m}^{-2} \right] \) and the fit of the geometric term \( f \) to thermodynamic and kinetic parameters is investigated by fitting and comparing the results to an ice nucleation measurement dataset of kaolinite \( \text{Welti et al., 2012} \). The section is followed by suggestions for criteria how to evaluate the quality of a CNT parameterization scheme (section 4.3). Finally in section 4.4 CNT parameters are estimated from experimental data for five different mineral dust types and afterwards in section 4.5 the criteria are tested for three CNT parameterization schemes and compared to an empirical parameterization.

### 4.1 Formulation of CNT for immersion freezing

The presence of IN immersed in supercooled droplets facilitates ice nucleation compared to homogeneous nucleation by providing a catalytic surface. The IN surfaces reduces the thermodynamic energy barrier \( \Delta G \) determined by \( T, S_i \) and \( \sigma_{iw} \). The difference in nucleation with and without an IN i.e. homogeneous or heterogeneous nucleation, is accounted for by the geometric term \( f \), also called wetting factor, compatibility factor or contact parameter. This term indicates the increased probability to nucleate a stable ice germ due to the presence of the IN surface and therefore reduced number of water molecules necessary to form an ice germ. It describes by how much the IN properties (of unknown nature) reduce the energy barrier for the formation of ice embryos on its surface compared to homogeneous freezing and can be expressed as a function of the contact angle \( \alpha \), which is the tangential angle between the ice embryo on the IN surface and the parent phase (here supercooled water) \( \text{Fletcher (1958)} \):

\[
\Delta G = f(\alpha) \cdot \Delta G_{\text{hom}} = f(\alpha) \cdot \frac{16\pi}{3} \cdot \frac{v_{\text{ice}}^2 \sigma_{iw}^3}{(k_B T \ln S_i)^2}
\]

with

\[
f(\alpha) = \frac{1}{2} \left[ 1 + \left( \frac{1 - X \cdot \cos \alpha}{g} \right)^3 \right] + X^3 \left( 2 - 3 \left( \frac{X - \cos \alpha}{g} \right) \right)
\]

\[
+ \left( \frac{X - \cos \alpha}{g} \right)^3 + 3 \cdot \cos \alpha \cdot X^2 \left( \frac{X - \cos \alpha}{g} - 1 \right)
\]

with
\[ X = \frac{r_{\text{IN}}}{r_{\text{germ}}} \quad \text{and} \quad g = \sqrt{1 + X^2 - 2 \cdot X \cdot \cos \alpha}, \]

where \( r_{\text{IN}} \) is the radius of the catalytic IN surface.

The contact angle \( \alpha \) has a value between \( 0^\circ \) and \( 180^\circ \), where the latter is equal to the case of homogeneous freezing (\( f=1 \)).

If the radius of the IN is significantly larger than the ice germ, radius curvature of the IN surface can be neglected leading to a simplified form of \( f \) (Volmer, 1939):

\[ f(\alpha) = \frac{(2 + \cos \alpha)(1 - \cos \alpha)^2}{4}. \quad (4.3) \]

Whereas the thermodynamic term in the nucleation rate \( J_{\text{imm}} \) (thermodynamic exponent determined by the energy barrier \( \Delta G \), see above) changes from homogeneous to heterogeneous freezing, the kinetic term is assumed to be the same for homogeneous and immersion freezing. The kinetics give the number of molecules, which can potentially be incorporated into the ice germ. They are captured in the prefactor of the nucleation rate (see Eq. 4.4) and the kinetic exponent (determined by the activation energy barrier \( \Delta g^b \)). The prefactor of the nucleation rate is different in the case of immersion freezing compared to homogeneous freezing. The difference is due to homogeneous freezing being a volume-dependent process while immersion freezing is assumed to be a surface dependent process. When calculating the non-equilibrium Zeldovich factor \( Z \), the freezing type has to be considered. \( Z \) is not the same for homogeneous and heterogeneous freezing, because the number of the water molecules in the ice germ, \( n_{k,\text{germ}} \), differs.

As shown in Pruppacher and Klett (2000), most of the prefactors cancel out in the case of heterogeneous freezing leading to the following expression for the nucleation rate for immersion freezing:

\[ J_{\text{imm}}[\text{m}^{-2} \cdot \text{s}^{-1}] = n_s \cdot \frac{k_B T}{h} \cdot \exp\left( \frac{\Delta g^b}{k_B T} \right) \cdot \exp\left( -\frac{f(\alpha) \cdot \Delta G}{k_B T} \right). \quad (4.4) \]

Figure 4.1 shows the difference in the homogeneous freezing rate compared to the immersion freezing rate (of kaolinite) on a logarithmic scale. \( J_{\text{imm}} \) is shifted to higher temperatures compared to \( J_{\text{hom}} \) and the curve is less steep due to the reduction of the energy barrier. This curve shift and flattening is described by the geometric term \( f \) and has to be captured by the different CNT formulations.
4.1 Formulation of CNT for immersion freezing

Figure 4.1: Comparison of the homogeneous freezing rate $J_{\text{hom}}$ and the immersion freezing rate $J_{\text{imm}}$ on a logarithmic scale and the corresponding energy barrier for the freezing process (at 250 K). The homogeneous nucleation rate $J_{\text{hom}}$ was calculated for a water droplet with a radius of 9 µm, which is the typical dropsize in the experimental setup IMCA. The immersion freezing nucleation rate $J_{\text{imm}}$ was calculated for kaolinite IN with a radius of 200 nm and a geometric term $f$ of 0.29. Note that $J_{\text{hom}}$ is defined per droplet, $J_{\text{imm}}$ per particle.
4 CNT for immersion freezing

4.1.1 Parameterization schemes for the geometric term $f$

Different schemes have been put forward to describe the influence of an IN on the nucleation process, i.e. to describe the ice nucleating surface properties of aerosol particles (Lüönd et al., 2010, Marcolli et al., 2007). Thus when fitting experimental data the fit parameter(s) describe the physical properties of the IN. Depending on the scheme these properties are represented by one or several fit parameters and the complexity for an implementation in a GCM differs accordingly. Note that increasing complexity normally comes with higher computational costs.

Three schemes including one or two fit parameters are used in the following sensitivity analysis (section 4.2) and briefly explained here. A graphical representation of each scheme is shown in Fig. 4.2. For more details see Marcolli et al. (2007) and Lüönd et al. (2010).

From immersion freezing measurements the frozen fraction $FF$ is obtained, which is the fraction of a droplet population/activated aerosol population that is frozen at a certain temperature $T$ after a certain time $t$. To compare different CNT based parameterization schemes to measurements, $FF$ is calculated from the nucleation rate $J_{imm}$. The frozen fraction $FF$ is given by:

$$FF = 1 - \exp(-J_{imm}(T, \alpha) \cdot A_{IN} \cdot \Delta t), \quad (4.5)$$

with $A_{IN}$ being the surface area of the IN. For simplicity particles are assumed to be spherical ($A_{IN} = 4\pi r_{IN}^2$). Thus, the surface used for the IN of specific mass represents a lower limit (non-spherical surface would be larger).

**Single-$\alpha$ scheme**

The single-$\alpha$ scheme is assigning one contact angle to the entire surface of each particle. It is based on the assumption that all particles have one common occurring surface property responsible for their ice nucleating ability. Consequently all particles have an equal probability to act as IN at given conditions. The scheme requires only one fit parameter ($f$ or $\alpha$).

It is the least complex and consequently the cheapest scheme suitable to implement in GCMs. However, it does not take into account that ice nucleating properties might be variable throughout a particle population. This scheme is used in several models (GCMs and parcel models), e.g. Barahona and Nenes (2009), Eidhammer et al. (2009), Ervens and Feingold (2012), Hoose et al. (2010), Khvorostyanov and Curry (2000, 2004, 2005), Liu et al. (2007), Morales Betancourt et al. (2012), Storelvmo et al. (2011).
4.1 Formulation of CNT for immersion freezing

\( \alpha \)-pdf scheme

The \( \alpha \)-pdf scheme is an extension of the single-\( \alpha \) scheme. It accounts for the heterogeneity of particles in an aerosol population by using a log-normal probability density function (pdf) for the contact angle \( \alpha \). The log-normal distribution of \( \alpha \) within a particle population is expressed by two fit parameters, the mean contact angle \( \mu \) and the variance \( \sigma \) of the distribution:

\[
p(\alpha) = \frac{1}{\alpha \sqrt{2\pi \sigma^2}} \cdot \exp\left(-\frac{\left(\ln(\alpha) - \mu\right)^2}{2\sigma^2}\right). \tag{4.6}
\]

This approach attributes an individual surface property to each particle on the entire particle surface.

The variance \( \sigma \) defines the heterogeneity of the particle property within the population: the larger the variance \( \sigma \), the larger the heterogeneity among the particles. The approach has been used to interpret freezing data, e.g. [Broadley et al. (2012), Ervens and Feingold (2012), Lüönd et al. (2010), Marcolli et al. (2007), Welti et al. (2012), Wheeler et al. (2014)], because it better represents the nature of the IN-sample. Due to the increased complexity compared to the single-\( \alpha \) scheme, only a few attempts have been made to implement it in GCMs [e.g. Wang et al. (2014)]. Application of the scheme in GCMs faces the problem of the unknown time evolution of the contact angle distribution. Because the most efficient IN will form ice first the remaining contact angle distribution (IN, which did not freeze yet) changes in case an aerosol population is not replenished within one timestep. Without an explicit treatment of the time evolution of the \( \alpha \)-pdf, ice formation will be overestimated since the most efficient IN can initiate freezing over and over again. Note that this issue is closely connected to the time resolution of the GCM, which is discussed in chapter 5.

The frozen fraction \( FF \) is derived by integrating the contact angle distribution over all possible contact angles:

\[
FF = 1 - \int_{0}^{\pi} p(\alpha) \cdot \exp(-J_{\text{imm}}(T, \alpha) \cdot A_{\text{IN}} \cdot \Delta t) \, d\alpha. \tag{4.7}
\]

Another extension and frequently used scheme is the active sites scheme, e.g. in Lüönd et al. (2010), Marcolli et al. (2007), Niedermeier et al. (2011), Welti et al. (2012), Wheeler et al. (2014). It goes one step further and assumes several surface sites on a single IN. Freezing is described based on active sites (initiating the nucleation process), which are randomly distributed on each IN surface within the particle population. As this scheme is computationally too expensive for the use in GCMs it is left out of the following analysis. More information about the active sites scheme can be found in Lüönd et al. (2010), Marcolli et al. (2007), Niedermeier et al. (2011).
Temperature dependent single-$\alpha$ scheme ($\alpha(T)$ scheme)

The $\alpha(T)$ scheme is a compromise between the single-$\alpha$ and the $\alpha$-pdf scheme. It does not take into account how contact angles are distributed among a particle population but it is assumed that $\alpha$ is different for different $T$, which reflects a change of the $\alpha$-pdf distribution and with that a change in $\mu$ with supercooling or time. This refers to the situation where good IN freeze first at highest temperatures shifting the mean contact angle $\mu$ of the remaining IN population to less efficient IN with further cooling (assuming the aerosol population does not substantially change while cooling and the contact angles are not replenished from one to the next timestep). The $\alpha(T)$ scheme is thus representing the shifted mean contact angle of an initial contact angle distribution. The temperature dependence of $\alpha$ can be approximated to be linear as discussed in Welti et al. (2012). This scheme is computationally cheaper compared to the $\alpha$-pdf scheme, because no integration over a contact angle distribution is necessary. It also circumvents the issue of shifting $\alpha$-pdf with time, as this is inherently captured in the scheme. Being capable to describe a variability of the freezing process due to a contact angle distribution without being computationally complex makes the $\alpha(T)$ scheme attractive for GCMs. However it demands an indirect assumption on how the aerosol population changes with time or supercooling, respectively.

The frozen fraction $FF$ is estimated analogously to the single-$\alpha$ scheme using a linear function for $\alpha(T)$:

$$FF = 1 - \exp(-J_{imm}(T, \alpha(T)) \cdot A_{IN} \cdot \Delta t),$$

with

$$\alpha(T) = \alpha_0 + m \cdot T.$$
4.2 Sensitivity analysis

4.2.1 Fitting immersion freezing measurements

In this section, the sensitivity of $J_{imm}$ and $FF$ to different combinations of $\sigma_{iw}$ and $\Delta g^\#$ (see chapter 3 for a discussion of these parameters) in combination with the contact angle schemes discussed in section 4.1.1 is analyzed by fitting and comparing the different CNT parameteri-
zation schemes to experimental data. This helps to understand how fit parameters influence the calculated $FF$ curves.

The experimental data taken from Welti et al. (2012) consists of optically detected frozen fractions $FF$ of droplets containing single immersed, monodisperse kaolinite (Fluka) particles. The data consists of $FF$ as a function of $T$, the particle radius $r_{IN}$ and the residence time in the measurement setup $t$. Experiments were performed using a CFDC (ZINC/IMCA) [see Welti et al. (2012) for more details]. The error bars of the data reflect the uncertainty in the distinction of water droplets and ice crystals in the detection unit. For the sensitivity analysis the dataset measured after 10 s for kaolinite particles with a diameter of 400 nm is used. Note that the size of the particles might be underestimated due to the assumption of sphericity and therefore the calculated nucleation rates $J_{imm}$ from experimental frozen fractions are always the lowest estimate.

To explore the sensitivity of $J_{imm}$ and $FF$ to thermodynamic and kinetic parameters of CNT we use different CNT formulations. The thermodynamic and kinetic parameters of CNT $\sigma_{iw}$ and $\Delta g^\#$ used here emerged from chapter 3. In the following all approaches and different CNT formulations, which are used for the analysis, are listed. An overview is given in Table 4.1. Capital letters indicate the author from whose publication thermodynamic and kinetic parameters are used.

#1: Single-$\alpha$ R&D + Z scheme

The first approach is to use a single-$\alpha$ scheme in combination with the thermodynamic and kinetic parameters shown to be in good agreement with homogeneous nucleation rates (see chapter 3). When using a single-$\alpha$ scheme it is important that the kinetic and thermodynamic parameters are a combination which reproduces the homogeneous data well as there is only one fit parameter and uncertainties cannot be compensated by additional parameters. The emerged best fitting combination of $\sigma_{iw}$ and $\Delta g^\#$ (derived independently of $J$) from the analysis of homogeneous data is $\sigma_{iw}$ from Reinhardt and Doye (2013) and $\Delta g^\#$ from Zobrist et al. (2007). It is tested if these formulations of $\sigma_{iw}$ and $\Delta g^\#$ are also applicable to reproduce heterogeneous nucleation rates with assumptions of the single-$\alpha$ scheme.

#2: Single-$\alpha$ R&D + fit $\Delta g^\#$ scheme

An second approach which emerged from Chen et al. (2008) is using a constant $\Delta g^\#$ as an additional fit parameter instead of taking a temperature dependent formulation. This assumption might be wrong in the context of homogeneous freezing especially at very low $T$ (Barahona, 2015). However, it should be applicable for immersion freezing as the change in $\Delta g^\#$ is small in the corresponding temperature range. The approach is used in combination with $\sigma_{iw}$ from Reinhardt and Doye (2013) and a single-$\alpha$ scheme. To
4.2 Sensitivity analysis

decide if $\sigma_{iw}$ from [Reinhardt and Doye (2013)] is the best choice, different expressions for $\sigma_{iw}$ (derived independently of $J$) are tested against a fit of $J_{\text{hom}}$ using constant $\Delta g^\#$ (see Fig. 4.7 analog to Fig. 3.17 in chapter 3). We find that $\sigma_{iw}$ from [Reinhardt and Doye (2013)] remains an appropriate choice even when $\Delta g^#$ is used as a constant.

#3 and #4 Single-$\alpha$ O + fit $\Delta g^#$ scheme and single-$\alpha$ E + fit $\Delta g^#$ scheme

For the sensitivity study of $J_{\text{imm}}$ to the kinetic and thermodynamic parameters the focus is on $\sigma_{iw}$. To capture the whole possible range, two formulations of $\sigma_{iw}$ are used. One from [Eadie (1971)] leading to the lowest homogeneous nucleation rate and a second formulation of $\sigma_{iw}$ from [Ouchi (1954)] leading to the highest homogeneous nucleation rate (see Fig. 4.7). For a summary of the two formulations of $\sigma_{iw}$ we refer to chapter 3. These two extremes of $\sigma_{iw}$ are used together with a constant $\Delta g^#$ (fit parameter) and the single-$\alpha$ scheme to clarify if a fit of $\alpha$ can compensate for a low/high $\sigma_{iw}$.

#5 $\alpha$-pdf R&D + Z scheme

This scheme is an $\alpha$-pdf scheme using the same thermodynamic and kinetic parameter as the single-$\alpha$ scheme (#1). This increases the complexity and adds an additional fit parameter compared to the single-$\alpha$ R&D + Z scheme (#1). By doing this we test the influence of the choice of the contact angle scheme on the fit result. Additionally we examine if the number of free fit parameters plays a role when choosing a contact angle scheme.

#6 $\alpha$-pdf E + Z scheme

One extreme formulation of $\sigma_{iw}$ from [Eadie (1971)] is used together with $\Delta g^#$ from [Zobrist et al. (2007)] and the $\alpha$-pdf scheme (see 5.).

#7 $\alpha(T)$ R&D + Z scheme

Similar to the $\alpha$-pdf R&D + Z scheme (#5), thermodynamic and kinetic parameter from the single-$\alpha$ scheme (#1) are used with an $\alpha(T)$ scheme instead of the single-$\alpha$ scheme.

The dataset from [Welti et al. (2012)] is fitted with the previous listed CNT formulations. The fits are done by least-square minimization of $FF$ as a function of $T$. The results are shown in Fig. 4.3 and Table 4.1. Table 3.1 additionally contains a summary of the CNT formulations. Overall most CNT formulations are able to capture the freezing curve well with similar root mean square errors (RMSE) of the estimated and measured freezing curve independent of the thermodynamic and kinetic parameters. In the following the results are discussed in more detail.
The single-\(\alpha\) R&D + \(Z\) scheme (#1) poorly captures the experimental data and results in a too steep freezing curve. With the single-\(\alpha\) scheme it is not possible to reproduce the reduction of the energy barrier in a correct manner and to decrease the temperature dependence of the nucleation rate from the homogeneous to the heterogeneous case. Having only one fit parameter, which in this case is a factor in the exponential term, is not sufficient to shift and flatten the freezing curve compared to homogeneous freezing. Only the \(T\)-shift of the freezing curve compared to homogeneous freezing is captured by the fitted single-\(\alpha\) scheme. This can be seen in a more general illustration in App. [4.B]. This result indicates that the simplified assumption of a homogeneous (single) contact angle for the entire population is not sufficient.

Using \(\Delta g^#\) as an additional fit parameter (scheme #2) reduces the steepness of the curve. In this case both fit parameters are factors in the exponential term of the nucleation rate with a similar influence on the fitted \(FF\). The fit parameter which is multiplied with the temperature dependent variable \(\Delta G(f)\) mainly shifts the freezing curve but cannot reduce the steepness sufficiently at the same time (see single-\(\alpha\) scheme). Using a second fit parameter \(\Delta g^#\) resolves this issue. A simplified view on this is, that one fit parameter is responsible for the shift, the other one for the flattening of the immersion freezing curve compared to homogeneous freezing. Using a constant \(\Delta g^#\) might be reasonable based on the results from the homogeneous freezing analysis (chapter [3]), but fitting \(\Delta g^#\) to immersion freezing data leads to substantially higher \(\Delta g^#\) than those estimated by theoretical calculations (see chapter [3]). Moreover the fit value of \(\Delta g^#\) is aerosol-specific. This might be an artificial result and it is questionable if the assumption of
4.2 Sensitivity analysis

a temperature independent and aerosol type specific (due to the fitting) $\Delta g^\#$ is a physical valid approach. It contradicts the assumption that the kinetic parameters such as $\Delta g^\#$ are the same for homogeneous and heterogeneous nucleation. The general approach to take the same thermodynamic and kinetic parameters (besides $f$ and the prefactor) for homogeneous and heterogeneous nucleation is based on the assumption that mechanisms in the supercooled water are not influenced by the immersed aerosol particle. This hypothesis might not be true. The aerosol might influence e.g. the diffusion of water molecules close to the particle which could explain a change in $\Delta g^\#$ depending on aerosol type.

Table 4.1: Overview of CNT formulations used for the sensitivity analysis, results for the fit parameters and evaluation of the fit result. The values are rounded to two digits after the decimal point.

<table>
<thead>
<tr>
<th>#</th>
<th>Formulation for $\sigma_{iw}$ and $\Delta g^#$</th>
<th>Contact angle scheme</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\sigma_{iw}$: Reinhardt and Doye (2013)</td>
<td>single-$\alpha$</td>
<td>Single-$\alpha$ R&amp;D</td>
</tr>
<tr>
<td></td>
<td>$\Delta g^#$: Zobrist et al. (2007) $5\times10^{-20}$ J</td>
<td>+ Z</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>$\sigma_{iw}$: Reinhardt and Doye (2013)</td>
<td>single-$\alpha$</td>
<td>Single-$\alpha$ R&amp;D</td>
</tr>
<tr>
<td></td>
<td>$\Delta g^#$: constant</td>
<td>+ fit $\Delta g^#$</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>$\sigma_{iw}$ from Ouchi (1954)</td>
<td>single-$\alpha$</td>
<td>Single-$\alpha$ O</td>
</tr>
<tr>
<td></td>
<td>$\Delta g^#$: constant</td>
<td>+ fit $\Delta g^#$</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>$\sigma_{iw}$ from Eadie (1971)</td>
<td>single-$\alpha$</td>
<td>Single-$\alpha$ E</td>
</tr>
<tr>
<td></td>
<td>$\Delta g^#$: constant</td>
<td>+ fit $\Delta g^#$</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>same as #1</td>
<td>+ fit $\Delta g^#$</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>$\sigma_{iw}$ from Eadie (1971)</td>
<td>single-$\alpha$</td>
<td>Single-$\alpha$ R&amp;D</td>
</tr>
<tr>
<td></td>
<td>$\Delta g^#$: constant</td>
<td>+ fit $\Delta g^#$</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>same as #1</td>
<td>+ fit $\Delta g^#$</td>
<td></td>
</tr>
</tbody>
</table>

An alternative to having $\Delta g^\#$ as an additional fit parameter is to use a more sophisticated contact angle scheme, e.g. the $\alpha(T)$ scheme (CNT #5 and #6) or the $\alpha$-pdf scheme (CNT #7). Both
approaches lead to good agreement with the experimental freezing curve and can be physically justified because they resemble the natural variability of IN by assuming a contact-angle distribution (in the case of $\alpha(T)$ only indirectly). The $\alpha(T)$ scheme has the disadvantage that it is not known how $\alpha$ changes with $T$. A wrong assumption could lead to an unphysical contact angle scheme, where the change of $\alpha$ does not represent the shift in the contact angle distribution correctly.

The curves resulting from scheme #3-7 (single-$\alpha$ + fit $\Delta g^\#$ schemes, $\alpha$-pdf schemes and $\alpha(T)$ scheme) all support the hypothesis that increasing the number of fit parameters from one to two allows to find a reasonable fit, independent of the kinetic and thermodynamic parameters chosen and also independently of the contact angle scheme. This hypothesis is also supported by the result of the single-$\alpha$ scheme, where one fit parameter alone cannot shift and flatten the freezing curve. However, using a single-$\alpha$ scheme with a different additional fit parameter (e.g. the slope of $\sigma_{iw}$ instead of a constant $\Delta g^\#$) does not lead to a better fit of the freezing curve. This might be due to the formula for the energy barrier preventing a sufficient influence of the additional fit parameter on the steepness of the curve. $\Delta g^\#$ as an additional fit parameter is able to reduce the steepness of the freezing curve as it has the opposite temperature dependence to the energy barrier $\Delta G$. For a visualization of how the fit parameters influence the freezing curve for each scheme see App.4.B.

Using one CNT formulation, e.g. the single-$\alpha$ R&D + fit $\Delta g^\#$ scheme (#2) together with wrong fit parameters emerging from a fit from a different CNT formulation, e.g. the single-$\alpha$ E + fit $\Delta g^\#$ scheme (#4) leads to a wrong freezing curve. This is illustrated in Fig. 4.3 [solid red line, single-$\alpha$ R&D + fit $\Delta g^\#$(E) (#2/4)].

Being able to reproduce experimental data does not directly depend on $\sigma_{iw}$ and $\Delta g^\#$ and not only on the number of fit parameters used, but also on the contact angle scheme. In a reverse conclusion this means that the fit results of $\alpha$, $\alpha_0$ and $m$ or $\mu$ and variance $\sigma$ strongly depend on the CNT formulation used. Looking at Table [4.1] one can see that $f$ differs substantially, e.g. when using the single-$\alpha$ + fit $\Delta g^\#$ scheme with different assumptions of $\sigma_{iw}$. Comparing $\sigma_{iw}$ from Reinhardt and Doye (2013) with $\sigma_{iw}$ from Ouchi (1954) leads to a difference in fitted $f$ of more than 300%, which translates into a difference in contact angle $\alpha$ of approx. 75°. However, all single-$\alpha$ + fit $\Delta g^\#$ schemes result in a nearly similar freezing curve with the same RMSE. The fit parameters from the contact angle scheme compensate inaccuracies coming from thermodynamic and kinetic parameters and thus mask potentially wrong assumptions, e.g. of the most important, unconstrained parameter in CNT of homogeneous freezing, $\sigma_{iw}$. This makes it challenging to compare fit parameters from different studies if not the same CNT formulation was used. Hence in the next subsection we investigate how fit results vary when thermodynamic and kinetic parameters differ and if there is a possibility to compare fit parameters from different studies using different CNT formulations.
4.2 Sensitivity analysis

4.2.2 Uncertainty of fitting \( \alpha \)

Table 4.1 shows that, dependent on the choice of \( \sigma_{iw} \) and \( \Delta g^\# \), the estimated fit parameters differ. The choice of thermodynamic and kinetic parameters (\( \sigma_{iw} \) and \( \Delta g^\# \)) influences the fit results of different contact angle schemes, which makes comparisons of studies difficult. A contact angle estimate can be different when using CNT with e.g. \( \sigma_{iw} \) from Pruppacher and Klett (2000) compared to using CNT with \( \sigma_{iw} \) from Zobrist et al. (2007). In this section the sensitivity of two contact-angle schemes to \( \sigma_{iw} \) and \( \Delta g^\# \) is investigated.

The two CNT formulations used in this analysis are a single-\( \alpha \) R&D + fit \( \Delta g^\# \) scheme (#2) and the \( \alpha \)-pdf R&D + Z scheme (#5) described above. We chose these two schemes because scheme #2 is used in GCMs and scheme #5 to interpret data. Both schemes contain two fit parameters (\( f \) and \( \Delta g^\# \) in scheme #2, \( \mu \) and variance \( \sigma \) of the contact angle distribution in scheme #5).

We analyze how these two fit parameters depend on a change in thermodynamic and kinetic parameters. For this purpose the thermodynamic and kinetic parameters are varied up to \( \pm 50\% \). For the scheme #2 the thermodynamic parameter \( \sigma_{iw} \) is varied, for the scheme #5 the thermodynamic and kinetic parameters \( \sigma_{iw} \) and \( \Delta g^\# \) are varied separately. The resulting fits are then compared to the reference fit results of section 4.2.1 (Table 4.1).

For each variation (e.g. an increase of \( \sigma_{iw} \) by 10\%) fitting is done to the same immersion freezing data from Welti et al. (2012) as in the previous section. Figure 4.4a) shows the relative change of the fit parameters as a function of percentual change in \( \sigma_{iw} \) for scheme #2. The higher the variation of \( \sigma_{iw} \) the larger is the deviation in \( f \) from the estimated fit parameters to the reference fit value, whereas \( \Delta g^\# \) remains unchanged. Fig. 4.4b) shows the relative change of the fit parameters as a function of percentual change in \( \sigma_{iw} \) and \( \Delta g^\# \) for scheme #5. In both cases a similar change in fit parameters can be seen. Changing the thermodynamic parameter \( \sigma_{iw} \) has a stronger impact on the fit parameters than changes in the kinetic parameter \( \Delta g^\# \) [see scheme #5 (Fig. 4.4b)]. This is expected from the nucleation rate formula, where \( \sigma_{iw} \) enters the calculation of the nucleation rate to the power of three and therefore changes the nucleation rate/frozen fraction more drastically than a change in \( \Delta g^\# \).

In case \( \sigma_{iw} \) is increased/overestimated, the fit parameters are decreasing to compensate the change (see dashed arrow in Fig. 4.4a) and conversely (see dotted arrow in Fig. 4.4a). The behavior of this compensation is not symmetric but follows the structure of the nucleation rate formula, i.e. \( 1/x \) dependence for \( f \) or \( \mu \) and variance \( \sigma \), respectively. That implies that the change in the fit parameter gets larger the larger the variation of \( \sigma_{iw} \) is. The relative change approaches -100\% with increasing \( \sigma_{iw} \). A larger deviation can be seen for the case where \( \sigma_{iw} \) is decreased/underestimated.

Note that in scheme #2 (Fig. 4.4a) only one fit parameter (\( f \)) is compensating the change in \( \sigma_{iw} \), which is due to the stronger impact of \( f \) than \( \Delta g^\# \) on \( J_{imm} \).
In case $\Delta g^\#$ is changed (only in Fig. 4.4b) the compensation is linear, following the structure of the nucleation rate formula.

Summarizing, an over/underestimation of $\sigma_{iw}$ has a strong effect on the value of the resulting fit parameter, while an over/underestimation of $\Delta g^\#$ is less severe. If fit parameters were estimated based on fitting different CNT formulations they cannot be directly compared. Fig. 4.4 can be used to estimate how different fit parameters would look like due to different assumptions for $\sigma_{iw}$ or $\Delta g^\#$. Some concrete examples/numbers how different fit parameter would look like if different CNT formulations are used for the fit are shown in Appendix 4.C.
4.2 Sensitivity analysis

Figure 4.4: Magnitude of deviation from a reference fit in percent (relative uncertainty). The results are shown for a variation of $\sigma_{iw}$ and $\Delta g^\#$ from 0 to $\pm$ 50%. The applied change is indicated by the line type (solid = change in thermodynamics, dashed = change in kinetics). The figure can be used to estimate the direction in which fit parameters deviate.
4.3 How to evaluate different CNT formulations?

The sensitivity analysis in section 4.2 raises the question how to evaluate different CNT formulations. Since most CNT formulations with at least two fit parameters are able to reproduce the freezing curve of the measurements, it is not possible to use this reproducibility or goodness of the fit as the only measure for the physical capability of the used CNT formulation. In practice, mostly, contact angle schemes are judged based on the RMSE of the estimated and measured freezing curve. Only looking at the reproducibility of freezing curves however might be not conclusive enough since the fit parameters can mask uncertainties in the thermodynamic and kinetic parameters of CNT. Therefore, the evaluation of different CNT formulations has to be done by stepwise testing different fit properties against measurements. The evaluation consists of a macroscopic and a microscopic perspective. Together, both perspectives yield three criteria.

At the macroscopic level: Is the CNT capable of reproducing the measured \( FF \) at a given temperature and how well is the IN size and time dependence captured? The primary factor to test is the representation of temperature dependence, followed by the size of the IN and the predicted time dependence of the freezing process. All three dependencies should be captured by a suitable CNT formulation if it is used as a function of \( T, r_{IN} \) and \( t \) in a GCM. When evaluating fits to measured freezing curves the goodness of the fit implicitly contains all three aspects (dependence on \( T, r_{IN} \) and \( t \)). However, because \( T \) has the strongest effect on the \( FF \), the goodness of fit mostly reflects how well the CNT scheme captures the temperature dependence.

Crit. 1 How accurately can the overall freezing curves be reproduced, i.e. how well is the temperature dependence of the \( FF \) captured by the CNT formulation?

Crit. 2 How accurately are the particle size and time dependence of the freezing process captured by the CNT formulation?

Criterion 2 can only be investigated if time and/or particle size dependent measurements are available.

At the microscopic level: Do the fit parameters match the microphysical assumptions of CNT, i.e. are the fit parameters physically reasonable? To evaluate if derived fit parameters are physically reasonable, the analysis of heterogeneous freezing can be combined with the findings from homogeneous freezing. Including homogeneous freezing into the analysis might be useful because of less unconstrained parameters in this case.

Crit. 3 Are the values for the fit parameters reasonable in the context of what we know about the microphysical process of nucleation?
In the following these three criteria are used to decide which CNT formulations are suitable for parameterizing immersion freezing, e.g. in a GCM.

4.4 Using experimental data to estimate CNT parameters for different contact angle schemes

In the following a comprehensive dataset of $FF$ (different aerosol species, aerosol particle sizes and residence times in the cloud chamber) is used. Five different mineral dust types were chosen for the analysis: Fluka kaolinite, illite-NX, montmorillonite, microcline (K-feldspar) and ATD (Arizona test dust). Montmorillonite or kaolinite are often used in global models as a surrogate for ice nucleating dust, e.g. montmorillonite in ECHAM6-HAM2. They both represent clay minerals with kaolinite being a rather inefficient clay IN and montmorillonite an efficient clay IN. Fluka Kaolinite, which was used here, has been widely used to study the mechanism of immersion freezing. Illite-NX was chosen by the INUIT community as a mineral dust reference sample, e.g. for instrument intercomparison (Hiranuma et al., 2014). Microcline (a sample from Namibia, variation Amazonit) and ATD were included to enable sensitivity studies of the freezing parameterization scheme with more efficient IN. The experiments were done by A. Welti (Welti et al., 2012 and personal communication) using size-selected aerosol particles with diameters of 50, 100, 200, 400, 800 and 920 nm and 10 s residence time. Additional kaolinite measurements were done for different residence times of 1, 2, 3, 6, 9 and 21 s. Note that the residence times are rounded to full seconds [compared to Welti et al. (2012)] and not all datasets include the smallest and/or largest size (kaolinite: 100 - 920 nm, illite 100 - 800 nm, montmorillonite 100 - 800 nm, microcline 50 - 800 nm, ATD 100 - 800 nm). The error bars of the data reflect the detection uncertainty and the statistical uncertainty in the measurement by multiple measurements.

To estimate the parameters of the CNT parameterization scheme four CNT formulations are chosen: #1 [single-$\alpha$ scheme], #2 [single-$\alpha$ scheme with $\Delta g$* as a fit parameter], #5 [$\alpha$-pdf scheme] and #7 [$\alpha(T)$ scheme]. For more details see Table 4.1. Scheme #3, #4 and #6 use a $\sigma_{iw}$, which was found not to represent homogeneous freezing well. The wrong assumption of $\sigma_{iw}$ was chosen on purpose for the sensitivity study in section 4.2.1 to demonstrate how that influences the fit results and the freezing curves. In the context of this section these formulations are excluded because they do not fulfill criterion 3. Note that also the single-$\alpha$ R&D + Z scheme (#1) is not expected to be able to reproduce the experimental freezing curves (criterion 1). It is still included here for comparison of the RMSE value with the other formulations (“bad” reference).

The fit parameters are determined by least square minimization of the calculated versus measured $FF$ from the dataset. For this purpose the dataset of each dust species, including all measurements as a function of $T$, aerosol particle size (diameter $d$) and residence time ($t$), is used. To get an impression of the variability of the fit parameters throughout a dataset, the kaolinite...
The fit parameters for the different CNT formulations and aerosol types are shown in Table 4.2 together with the best fit root mean square error (RMSE). The fit curves in comparison to the measured FF are shown in Fig. 4.5 to Fig. 4.6 (in the case of kaolinite only a selection of the data is shown).

<table>
<thead>
<tr>
<th>#</th>
<th>Fit parameter</th>
<th>Kao RMSE</th>
<th>Ill RMSE</th>
<th>Mont RMSE</th>
<th>Micro RMSE</th>
<th>ATD RMSE</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$f$</td>
<td>0.56</td>
<td>0.2</td>
<td>0.61</td>
<td>0.17</td>
<td>0.56</td>
<td>0.18</td>
</tr>
<tr>
<td>2</td>
<td>$f$</td>
<td>0.29</td>
<td>0.14</td>
<td>0.36</td>
<td>0.17</td>
<td>0.28</td>
<td>0.09</td>
</tr>
<tr>
<td>3</td>
<td>$\Delta g / 10^{20}$ J</td>
<td>9.95</td>
<td>8.93</td>
<td>10.03</td>
<td>11.97</td>
<td>12.58</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>$\mu$/rad</td>
<td>0.5</td>
<td>0.09</td>
<td>0.54</td>
<td>0.13</td>
<td>0.05</td>
<td>0.11</td>
</tr>
<tr>
<td>5</td>
<td>$\sigma$ rad</td>
<td>0.06</td>
<td>0.05</td>
<td>0.13</td>
<td>0.04</td>
<td>0.04</td>
<td>0.11</td>
</tr>
<tr>
<td>6</td>
<td>$\alpha_0$/rad</td>
<td>0.84</td>
<td>0.14</td>
<td>0.98</td>
<td>0.13</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>7</td>
<td>$m$ $\alpha_0$</td>
<td>-0.02</td>
<td>-0.02</td>
<td>-0.02</td>
<td>-0.03</td>
<td>-0.04</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.2: Estimated fit parameters for the different CNT formulations used for different mineral dust types. The values are rounded to two digits after the decimal point.

The geometric term $f$ in Table 4.2 is smallest for microcline, showing that this is the most efficient IN investigated here. The second lowest value for $f$ is found for ATD. Montmorillonite and kaolinite seem to be quite similar in terms of IN efficiency, whereas illite is the least efficient IN.

Revising the fit results with criterion 1 shows that scheme #1 is too steep and not able to reproduce experimental data, resulting in a high RMSE. One fit parameter is not enough to shift and reduce the steepness of the immersion freezing curve sufficiently compared to homogeneous freezing. Thus the single-\(\alpha\) scheme #1 does not fulfill criterion 1.

Reasonable fit results (low RMSE) are obtained with scheme #2 and #5 for all datasets. It is difficult to fit the data with scheme #7 since there is more than one solution for fit parameters (no absolute minimum of the fitting function). However, $a_0$ should not become negative and $m$ has to be negative so that $\alpha$ increases with decreasing $T$. Otherwise criterion 3 is not fulfilled. Here only the fit parameters that fulfill criterion 3 are given (local minimum of the fitting function). Over all CNT formulations, the fits with largest RMSE are the ones for ATD which is probably caused by the mixed mineralogy of ATD. The capability of the different CNT formulations to best reproduce immersion freezing varies from dust to dust. Therefore, we establish a ranking for each dataset similar to the methodology of Wheeler et al. (2014). The best CNT formulation gets a ranking of 1, the worst a ranking of 4. From the ranking of the different datasets an average score is estimated to judge the overall capability to predict FF for each CNT formulation. The ranking (see Table 4.3) shows that scheme #7 and scheme #2 are the best followed by scheme #5 and scheme #1. Calculating the average RMSE from all fits (as an alternative) leads to a similar result, where the scheme #7 is the best and scheme #1) the worst (see also Table 4.3).
4.4 Using experimental data to estimate CNT parameters

**Figure 4.5:** Calculated FF of kaolinite for certain times and sizes using scheme #2, scheme #5 and scheme #7 with corresponding fit parameters (see Table 4.2) and a simplified immersion freezing parameterization scheme based on Niemand et al. (2012) compared to the dataset. Figure (a)-(c) show the particle size dependence (t=10 s), Fig. (c)-(e) show the time dependence (d=400 nm).
Note that this ranking does not consider criterion 3 and is only based on fit statistics. It also does not show directly how good the CNT formulations reproduce time and particle size dependence of the freezing process (criterion 2).

<table>
<thead>
<tr>
<th>#</th>
<th>Kaolinite</th>
<th>Illite</th>
<th>Montmorillonite</th>
<th>Microcline</th>
<th>ATD</th>
<th>Average score</th>
<th>Average RMSE</th>
<th>Score based on average RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>4</td>
<td>3.2</td>
<td>0.218</td>
<td>4</td>
</tr>
<tr>
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<td>1</td>
<td>2</td>
<td>1.6</td>
<td>0.136</td>
<td>2</td>
</tr>
<tr>
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<td>1</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>1.8</td>
<td>0.15</td>
<td>3</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1.2</td>
<td>0.118</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 4.3: Ranking of the capability of the different CNT formulations to reproduce the freezing curves for different mineral dust particles.

In section 4.5, the time and size dependence of the best three CNT formulations (scheme #2, scheme #5 and scheme #7) are compared to the kaolinite dataset. A deterministic immersion freezing parameterization scheme based on Niemand et al. (2012) is included in the evaluation for comparison (for more details see Appendix 4.E). This scheme is frequently used in literature for comparing laboratory measurements, e.g. Atkinson et al. (2013), Hoffmann et al. (2013), Kanji et al. (2013), O’Sullivan et al. (2014), Tobo et al. (2014), Umo et al. (2015), but also as a parameterization scheme in some cases, e.g. Barahona et al. (2014), Hande et al. (2015), Paukert and Hoose (2014b).
4.4 Using experimental data to estimate CNT parameters

Figure 4.6: Calculated FF of illite, montmorillonite, microcline and ATD after a residence time \( t \) of 10 s for certain sizes using the single-\( \alpha \) R&D + fit \( \Delta g^\# \) scheme (#2), the \( \alpha \)-pdf R&D + Z scheme (#5) and the \( \alpha(T) \) R&D + Z scheme (#7) with corresponding fit parameters (see Table 4.2) and a simplified immersion freezing parameterization scheme based on Niemand et al. (2012) compared to the dataset.
Figure 4.6: Continued.
4.5 Testing the time and particle size dependence (Criteria 2)

To test the ability of the single-\(\alpha\) R&D + fit \(\Delta g^\#\) scheme (#2), the \(\alpha\)-pdf R&D + Z scheme (#5) and the \(\alpha(T)\) R&D + Z scheme (#7) to reproduce experimentally observed size and time dependence, the fit parameters for kaolinite (see Table 4.2) are used to calculate FFs for three different residence times (1, 10 and 21 s) and three different aerosol diameters (100, 400, 800 nm). In the case of the size dependent calculation of FF the time is 10 s, in the case of the time dependent calculation the diameter is 400 nm. The calculated FF is compared to measurements of the size and time dependent FF in Fig. 4.5. The analysis of the RMSE for each dataset and CNT formulation revealed marginal differences in the second decimal place and is therefore not shown.

Figure 4.5 shows that scheme #5 is able to represent the time and particle size dependence better than scheme #2 and #7. This leads to an overall smaller RMSE and explains the better ranking for scheme #5 in the case of kaolinite (see Table 4.2). Looking at Fig. 4.5 the scheme #2 and #7 seem to overpredict both the size and time dependence, while scheme #5 seems to underpredict the particle size dependence but captures the time dependence well. Overpredicting the size dependence translates into an overestimation of FF for particles with an aerosol particle diameter larger than 400 nm and an underestimation of FF for particles with an aerosol particle diameter smaller than 400 nm. Underpredicting the size dependence has the opposite influence on FF. Overpredicting the time dependence means that FF is overestimated having a larger timestep (larger 10 s) as in GCMs.

Note, that the outcome of the evaluation depends on the dataset used. For different aerosol species the ranking of scheme #5 and scheme #2 differs, e.g. for montmorillonite, microcline and ATD. Due to this limitation, it cannot generally be concluded which contact angle scheme better fulfills criterion 2. Since all three schemes are computationally equally expensive (if the contact angle distribution is not changed with time), they all might be chosen for CNT based immersion freezing parameterization schemes in GCMs.

In Fig. 4.5 the CNT curves are also compared to an empirical immersion freezing parameterization scheme based on the expression given in Niemand et al. (2012). Since the scheme is dependent on the measurement data used to derive it, the use for comparison is only limited. To be able to compare an empirical scheme to the CNT schemes, a \(n_{\text{IN}}\) scheme similar to the one in Niemand et al. (2012) was fitted to kaolinite measurements. Details can be found in Appendix 4.E. The \(n_{\text{IN}}\) scheme slightly overestimates the particle size dependence and the scheme does not capture any time dependence since it is deterministic. It is able to represent freezing curves in a similar manner as CNT. However, due to the general characteristics of empirical relations it is not clear if it can be extrapolated to a wide \(T\)-range, which would be mandatory for the use in a GCM.
4.6 Conclusion and outlook

In this study the sensitivity of CNT based immersion freezing parameterization schemes to thermodynamic and kinetic parameters is investigated as a response to the large sensitivity of homogeneous freezing on these parameters. For the use in models a validation of these sensitivities is important to estimate uncertainties coming from different parameterization schemes which include the effect of aerosol particles on the energy barrier of ice nucleation.

Compared to homogeneous freezing, immersion freezing has one more unconstrained parameter, namely the contact angle $\alpha$. Different schemes to represent the contact angle/–distribution with one or two fit parameters based on experimental data are tested. It is found that several different contact angle schemes are able to reproduce the experimental freezing curve. These schemes contain two fit parameter, while the contact angle scheme with only one fit parameter, the single-$\alpha$ scheme, cannot reproduce the freezing curves.

Analyzing the importance of the choice of $\sigma_{iw}$ and $\Delta g^#$ to parameterize immersion freezing revealed that uncertainties in the thermodynamics or kinetics can be compensated by two-parameter contact angle schemes. As a result an under/overestimation of $\sigma_{iw}/\Delta g^#$ does not lead to a bad representation of freezing curves as in case of homogeneous freezing. Because the fit parameters compensate inaccuracies or uncertainties of the thermodynamic and kinetic parameters, the absolute value of the found fit parameters is highly dependent on the choice of thermodynamic/kinetic parameters within the formulation of CNT (especially on $\sigma_{iw}$). As a consequence, contact angles for CNT parameterization schemes from different authors can only be applied within the same CNT formulation. Implementing one formulation of CNT into a GCM together with a different estimate for $\alpha$ might introduce an offset into modeling studies (see red curve in Fig. 4.3). Besides the sensitivity of $\alpha$ on the thermodynamic and kinetic parameters used in CNT makes a direct comparison of contact angle values derived in different studies impossible. It again stresses the importance of highlighting which CNT formulation was used for the analysis of experimental data (as stressed in chapter 3).

Another consequence is that the reproducibility of freezing curves should not be the only criterion to decide on a CNT formulation because it can be misleading if the formulation has at least two fit parameters. Therefore some criteria to evaluate reasonable CNT formulations are compiled here. They additionally take into account the microphysical perspective (assumptions the CNT formulation is based on) and the ability to predict the size and time dependence of the freezing process. Particle size and nucleation time are implicitly included in the reproducibility of freezing curves but should be evaluated separately.

The fit parameters for scheme #2, scheme #5 and scheme #7 are determined for five different datasets of mineral dust (kaolinite Fluka, NX illite, montmorillonite, microcline and ATD) by fit-
4.6 Conclusion and outlook

ting the CNT approach to the FF from measurements. Good results in reproducing the freezing curves (criterion 1: $T$-dependence and partly 2: size and time dependence) are achieved when using a single-$\alpha$ scheme with fitted constant $\Delta g^\#$ (CNT #2), an $\alpha$-pdf scheme (CNT #5) or an $\alpha(T)$ scheme (CNT #7) when ignoring unreasonable solutions for the fit parameters (criterion 3). The single-$\alpha$ scheme does not perform well when $\Delta g^\#$ is not used as an additional fit parameter. The three good working CNT formulations (#2, #5 and #7) are further evaluated by looking how well they reproduce the time and particle size dependence of the kaolinite dataset (criterion 2). In this case the $\alpha$-pdf scheme (CNT #5) works better, as it captures the time dependence. However, the particle size dependence is underpredicted. Using a single-$\alpha$ scheme with fitted constant $\Delta g^\#$ (CNT #2) or an $\alpha(T)$ scheme (CNT #7) overpredicts the size and time dependence. Note that the results only refer to the kaolinite dataset. Due to this restriction it remains ambiguous which CNT formulation best fulfills criterion 2 and thus is best suited for modeling purpose. It would be helpful to redo the analysis for other dust types. From the perspective of criterion 2 all three CNT formulations seem to be able to predict nucleation rates for mineral dust particles.

An empirical immersion freezing parameterization scheme [based on Niemand et al. (2012)] can also capture the freezing curves and IN size dependence quite well. However, it is not clear if it is legitimate to extrapolate the empirical relationship, so that the full $T$-range is covered. Criterion 3 is difficult to evaluate coming from a macroscopic level as microphysical knowledge is missing at this point. Scheme #5 is consistent with the microphysical perspective of freezing. Evaluating scheme #2 requires knowledge about a possible influence on $\Delta g^\#$ by an aerosol particle immersed in the supercooled droplet and is thus not possible. Scheme #7 can return unphysical fit parameters (criterion 3 is not always fulfilled). However, this evaluation is limited by the recognition how $\alpha$ might change with temperature.

More size and time dependent measurements of different IN would be beneficial to evaluate different CNT formulations more robustly.
4.A Evaluation of the different formulations of $\sigma_{iw}$ together with a constant value for $\Delta g^\#$ against homogeneous freezing data.

Figure 4.7: Comparison of the fitted $J_{hom}(T)$ (solid black line) with calculated nucleation rates using different formulations of $\sigma_{iw}$ and constant values for $\Delta g^\#$. Grey dots show the collected homogeneous freezing dataset. $\sigma_{iw}$ from Reinhardt and Doye [2013] captures the homogeneous freezing curve the best.
4.B Analysis of the different contact angle scheme formulations: How do the fit parameters influence the calculated nucleation rate/frozen fraction.

![Diagram showing nucleation rate and frozen fraction](image)

Figure 4.8: Nucleation rate $J_{imm}$ and frozen fraction $FF$ in dependence of the fit parameters for the different contact-angle schemes (here $f$ and $\Delta g^\#$).

In case of the single-$\alpha$ R&D + fit $\Delta g^\#$ scheme (#2) the geometric term $f$ was chosen to be 0.4. Note that the dependence of the scheme (in the case of a fixed $\Delta g^\#$) on $f$ is the same as with the single-$\alpha$ R&D + Z scheme (#1).

Decreasing $f$ (reducing the energy barrier) shifts the freezing curve to warmer temperatures. The slope changes only negligible. Increasing $\Delta g^\#$ (increasing the activation energy barrier) shifts the freezing curve to lower temperatures. It also changes the slope of the curve - a higher activation energy barrier leads to a flattening of the curve.
Figure 4.9: Nucleation rate \( J_{\text{imm}} \) and frozen fraction \( FF \) in dependence of the fit parameters for the different contact-angle schemes (here \( m \), \( \mu \) and \( \sigma \)).
In case of scheme #7 \( \alpha_0 \) was chosen to be 1.5 (\( \approx 85^\circ \)). Note that the dependence of the scheme (in the case of a fixed change in contact angle \( m \)) on \( \alpha_0 \) is the same as the change with \( f \) of the single-\( \alpha \) R&D + Z scheme (#1).
In case of the \( \alpha \)-pdf R&D + Z scheme (#5) \( \sigma \) was chosen to be 0.01 in the left figure, \( \mu \) was chosen to be 0.3 (\( \approx 18^\circ \)) in the right figure.
Decreasing \( m \) (contact angle gets larger with \( T \) because most efficient IN are used first) shifts the freezing curve to colder temperatures and changes the slope of the curve (flattening).
Increasing \( \mu \) (increasing the contact angle) shifts the freezing curve to lower temperatures and flattens the curve, while an increase in \( \sigma \) (broadening of the contact angle distribution) changes the slope of the freezing curve only (flattening). Note that already small changes in \( \mu \) lead to a considerable shift of the curve compared to the other schemes.

Figure 4.4 can be used to estimate the deviation of fit parameters from different CNT formulations relative to each other. To show this we estimate the difference in fit parameter when using $\sigma_{iw}$ from Eadie (1971) instead of Reinhardt and Doye (2013) in combination with an $\alpha$-pdf scheme [scheme (6) compared to scheme (5)].

Within the 10 K temperature range of the immersion freezing measurements (236-246 K) $\sigma_{iw}$ is on average 4% higher when using $\sigma_{iw}$ from Eadie (1971) instead of Reinhardt and Doye (2013). An increase in $\sigma_{iw}$ by 2.5% (246 K) or 5% (236 K) would lead to a decrease in $\mu$ by approximately 7 to 13% (see Fig. 4.4 b). Now we check if that estimated change matches with the real change when fitting the same dataset with the two different $\sigma_{iw}$. In Table 4.1 using $\sigma_{iw}$ from Eadie (1971) leads to a mean contact angle of 0.44 rad (approx. 25.5°) instead of 0.5 rad (approx. 28°) when using $\sigma_{iw}$ from Reinhardt and Doye (2013). This is a difference of 12%, conform with the estimate from Fig. 4.4 (approx. 7-13%). However, the variance $\sigma$ of the $\alpha$-pdf distribution is expected to change less (5 to 9%) but a change by 25% is found.

In some cases the predicted change in fit parameters from Fig. 4.4 deviates from the real change in fit parameters (Table 4.1). The problem with Fig. 4.4 is, that the assumption of a constant variation of $\sigma_{iw}$ is invalid in most cases, so that Fig. 4.4 can not be used easily. However, it can be used to illustrate how fit results might change and estimate a rough deviation from the reference when using different thermodynamic and kinetic parameters especially for cases where $\sigma_{iw}$ changes nearly constant over the fitted temperature range. This can help when comparing fit results to fit results from another study where a different formulation of CNT was used.
4. D Variability of the fit parameters throughout one dataset.

The variability of the fit parameters throughout the dataset can be seen when fitting the single-$\alpha$ R&D + fit $\Delta g^*$ scheme (#2) and the $\alpha$-pdf R&D + Z scheme (#5) to $FF$ of kaolinite data for different sizes and residence times separately. The resulting fit parameters are compared in Fig. 4.11 for different sizes in red and for different times in blue and light blue. Each point in Fig. 4.11 represents the value of the best fit parameter for one subset of the kaolinite dataset. The labels on the x-axis give information which subset of the dataset was fitted. The residence time is 10 s for the data subsets of different sizes and the diameter of the kaolinite particles 400 nm or 800 nm for the data subsets of different times (blue/light blue). The dashed line indicates the mean of the size or time dependent fit parameter. The standard deviation is shown as shaded box.

The fit parameters vary depending on the measurement conditions. Omitting the measurement with the smallest aerosol particle size ($d=100$ nm) and the shortest residence time (1 s) the variation between the data subsets is small. The variability of the fit parameters is larger for different aerosol particle sizes compared to different residence times, which might be due to the higher sensitivity of the freezing process to particle size compared to time. For scheme #2 the fit parameters seem to be correlated. High values of one fit parameter, e.g. $f$, correspond to low values of the other fit parameter, e.g. $\Delta g^*$. Scheme #5 on the other hand does not show a clear correlation.

The different fit results for scheme #5 can be used to study how the shape of the contact angle distribution might change with the size of the particles or the residence time.

Whereas the fitted contact angle distribution does not change noticeable with time between 1 and 21 s (Figure not shown here), the variance $\sigma$ changes with particle size (see Fig. 4.10). The contact angle distribution broadens with increasing aerosol particle size (neglecting the fit of the 400 nm dataset, which does not fit into the picture), which reflects a larger probability of different $\alpha$ on the aerosol particle population with increasing size. The particle population is more heterogeneous. Additionally the maximum is shifting to the left (smaller contact angle) which means that the IN is getting more efficient with size. Note that the curves are not considering measurement uncertainties of the fitted data and therefore can only used to qualitatively interpret the result. In case of idealized measurements the result could be used to derive a relationship for the width of the contact angle distribution and the size of the IN.
4.D Variability of the fit parameters throughout one dataset

Figure 4.10: Change of $\alpha$-pdf with particle size for the kaolinite dataset. The residence time is 10 s.

Figure 4.11: Variability of the fit parameters throughout the kaolinite dataset. The variability with the aerosol particle size ($d$) is shown for a residence time $t$ of 10 s (red). The variability with the time ($t_1$ and $t_2$) is shown for a aerosol particle diameter of 400 nm ($t_1$, blue) and 800 nm ($t_2$, lightblue). The first row shows the fit results for scheme #2, the second row for scheme #5. The RMSE value shows the deviation of the fit to the single dataset it was fitted to.
**Uncertainty of fit parameters due to limited data**

In many cases there are not size- and time-dependent measurements available. Here we investigate the quality of fit parameters if only limited amount of data is available. For that purpose we use the kaolinite dataset (as this is the most thoroughly dataset available within this study) and use only subsets of the dataset assuming that not all data is available to estimate the fit parameters. The quality of the gained fit parameters is then estimated by using the complete dataset and look how good the freezing curves can be represented (RMSE). We look at four different cases:

1. Reference, the whole dataset is fitted (see also Table 4.2).

2. Only size dependent measurements are available, time dependence is not known ($t=10$ s).

3. Only time dependent measurements are available, size dependence is not known ($d=400$ nm).

4. Only one measurement is available ($t=10$ s, $d=400$ nm).

The resulting fit parameters and the deviation from the kaolinite dataset is shown in Table 4.4.

<table>
<thead>
<tr>
<th>#</th>
<th>Fit parameter</th>
<th>Reference</th>
<th>RMSE</th>
<th>Only</th>
<th>RMSE</th>
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<td>11.01</td>
<td></td>
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</tr>
<tr>
<td>5</td>
<td>$\mu$/rad</td>
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<td>0.5</td>
<td>0.09</td>
<td>0.49</td>
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<td>$\sigma$</td>
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<td>0.05</td>
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<td>0.07</td>
<td>0.04</td>
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</table>

Table 4.4: Estimated fit parameters for the different CNT formulations used for kaolinite using the complete dataset or subsets of the dataset. The values are rounded to two digits after the decimal point. The RMSE value shows the deviation of the fit to the complete dataset.

The fit parameters are not significantly different when the dataset is limited to only size or only time dependent data. Also the deviation from the complete dataset is not significant (RMSE). This analysis therefore does not allow any conclusion how many dependencies, e.g. size and time, have to be taken into account to successfully fit freezing curves. However if using only one single dataset, the results for the fit parameters are different and the deviation from the measurements is higher. Note that the deviation when fitting only a single dataset could be larger if a dataset is chosen which is not similar to the average values of the dataset as in this case. This means that there is no guarantee that fits can be extrapolated/used in a universal way across different conditions.
4.E Estimating the surface site density $n_{s,\text{IN}}$

The Niemand et al. (2012) scheme for immersion freezing of natural dust, is a deterministic scheme based on the approach of Connolly et al. (2009) and AIDA measurements. A detailed description can be found in chapter 2.2.

The ice active surface site density of natural dust is described by the following equation:

$$\begin{align*}
n_{s,\text{IN}}(T) &= b \cdot \exp(-A \cdot a \cdot (T - 273.15 \text{ K}) + B), \\
\end{align*}$$

(4.9)

with the fit parameters $A = -0.517$ and $B = 8.934$ and the unit correction factors $a = \text{K}^{-1}$ and $b = \text{m}^{-2}$. Based on this ice active surface site density $FF$ can be calculated:

$$\begin{align*}
FF &= \frac{N_{i,j}}{N_{\text{tot},j}} = 1 - \exp(-A_j \cdot n_{s,\text{IN}}(T)). \\
\end{align*}$$

(4.10)

Eq. 4.9 was used here to fit the dataset for the different mineral dust types. The fits were done in two different ways: By using Eq. 4.10 and Eq. 4.9 to fit the measured $FF$ or by using Eq. 4.10 to convert the $FF$ measurements to surface site densities and fit $n_{s,\text{IN}}(T)$ directly following Eq. 4.9. The results are show in Table 4.5 and in Fig. 4.12. The scheme is labeled “$n_{s,\text{IN}}$” in Fig. 4.5 and 4.6.

Table 4.5 shows that the results for the fit parameters are very different depending on whether the $FF$ is fitted or the active site density $n_{s,\text{IN}}$ directly. That is due to the characteristics of the freezing curve. The very small $FF$ at warm temperatures and limited $FF$ (to 1) at low temperatures leads to a flattening of the $n_{s,\text{IN}}$ curve. Calculating $n_{s,\text{IN}}$ at low temperatures from $FF$ close to 1 gives the number of active sites, which was needed to freeze all droplets. However it could be that more active sites were present than needed to freeze all droplets. Therefore the tail (low and high $FF$) of the $FF$ dataset is often left out of the fitting. Here we investigate how the fit results and the freezing curves change depending on the share of the dataset accounted for fitting. We use the complete dataset as a first step and then omit $FF$ data higher than 0.9 and lower than 0.1 and 0.8 and 0.2, respectively. Figure 4.13 shows this exemplary using the dataset of kaolinite particles. It can be seen in Fig. 4.13b that the surface site density $n_{s,\text{IN}}$ is quite different depending on how it is estimated. The variation in $n_{s,\text{IN}}$ depending on the share of the $FF$ dataset is larger when $n_{s,\text{IN}}$ is estimated directly by fitting to calculated $n_{s,\text{IN}}$ from $FF$ measurements. The largest deviation from all other fits originates when $n_{s,\text{IN}}$ is estimated directly taking all data into account. Cutting away the tail of the $FF$ measurements leads to a very similar result when $n_{s,\text{IN}}$ is estimated directly (black solid line) compared to the indirect estimate of $n_{s,\text{IN}}$ using the complete $FF$ data (red dashed line). The implication of the different estimations for $n_{s,\text{IN}}$ is shown in Fig. 4.13c for an example dataset of kaolinite ($d=400$ nm,
4 CNT for immersion freezing

t=10 s). The freezing curves from the indirect $n_s,\text{IN}$ fit are not so different from each other and capture the measurements quite well. When cutting away the tail of the $FF$ data ($FF > 0.2$ and $FF < 0.8$) also the freezing curve based on the direct estimated $n_s,\text{IN}$ captures the data well and falls on the freezing curve of the indirect $n_s,\text{IN}$ using the same share of $FF$ data. It seems necessary to cut the tails away from the $FF$ data when $n_s,\text{IN}$ is fitted directly. When estimating $n_s,\text{IN}$ indirectly by using $FF$ it seems that there is no need for cutting the tail. Not cutting the tail increases the amount of data available for the fitting and might therefore be preferable. However, very low/high $FF$ are most susceptible to experimental uncertainties, which could be a legitimation of cutting the tail away from the dataset. Because the results are different depending on the methodology this sensitivity should be taken into account when comparing different $n_s,\text{IN}$ from literature. Maybe an uniform standard on how to derive $n_s,\text{IN}$ could help.

<table>
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<th>Mont</th>
<th>Micro</th>
<th>ATD</th>
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Table 4.5: Estimated fit parameters for the deterministic $n_s,\text{IN}$ approach for different mineral dust types. The values are rounded to two digits after the decimal point.
4.E Estimating the surface site density \( n_{s,IN} \)

Figure 4.12: Surface site density \( n_{s,IN} \) of different mineral dust types. The points are calculated surface site densities from FF measurements, the lines are the corresponding fits. Some estimates of \( n_{s,IN} \) found in literature are added.

Figure 4.13: Sensitivity study of different methods to estimate the surface site density \( n_{s,IN} \) of kaolinite and its implications.
ECHAM6-HAM2: Model description and technical description of freezing scheme

ECHAM6-HAM2 is the GCM used in this thesis to test different immersion freezing parameterization schemes. The model is introduced in this chapter including an illustration of the cloud and aerosol scheme HAM2. It is followed by a section about the implementation of the new parameterization schemes, where essential questions are discussed.
5 ECHAM6-HAM2

5.1 Overview of the model

The ECHAM6-HAM2 global climate model used in this thesis consists of the general circulation model (GCM) ECHAM6 coupled to the aerosol module HAM2.

ECHAM6 is based on the European Centre for Medium-range Weather Forecasts (ECMWF) weather forecast model and has been further developed at the Max Planck Institute for Meteorology (MPI) in Hamburg. As a GCM it describes the atmospheric transport of air masses, energy, moisture and trace gases within these air masses by using transport equations. These equations, including advection, convection and small scale turbulences, represent the dynamical state of the atmosphere. Additionally physical processes such as radiation, surface processes and cloud and precipitation formation are represented in the model through parameterizations. The dynamical core of the model is pseudo-spectral. The linear terms such as the prognostic equations for temperature, surface pressure, divergence and vorticity are evaluated on a spectral grid with triangular truncation. The non-linear terms (including parameterizations) are solved on a Gaussian grid after a coordinate transformation.

The standard horizontal resolution of ECHAM6 is T63, which translates to $1.875^\circ \cdot 1.875^\circ$. The vertical dimension is discretized using hybrid coordinates, which is a combination of pressure and sigma coordinates. The standard vertical resolution of ECHAM6 is 47 levels (L47) with the highest level at 0.01 hPa, which is at approximately 80 km of height.

More information about ECHAM6 and the dynamical core can be found in Stevens et al. (2013). Sophisticated parameterizations for cloud microphysics and aerosol-cloud interactions are described in HAM2, the aerosol part of the model. This part is responsible for interactive aerosol particles and cloud microphysics. HAM2 contains a two-moment cloud microphysics scheme (Lohmann and Hoose, 2009) and the two-moment aerosol microphysics model M7 (Stier et al., 2005). M7 is capable of simulating the time evolution of multi-component size resolved aerosol populations (Vignati et al., 2004). The aerosol numbers/masses are characterized as a set of log normal distributions. The median diameter is calculated based on number and mass of the aerosol mode. The use of seven aerosol modes enables to describe different mixing states of aerosol particles (see section 5.2). Thus aerosol particles can be characterized by mass, particle size, solubility and composition.

Microphysical processes, which are captured by HAM2, are phase changes of water (condensation, evaporation, deposition, sublimation, freezing, melting), precipitation processes such as aggregation, accretion (collision-coalescence of cloud droplets with raindrops, collision of snowflakes with ice crystals, riming) and autoconversion, transformation processes of precipitation such as melting and sublimation of snow and evaporation of rain and diffusional growth of ice crystals (Wegener-Bergeron-Findeisen process).

The stratiform cloud scheme within HAM2 adds four additional prognostic variables to the output of ECHAM6-HAM2, which are the mass and number of cloud water and cloud ice.
droplet number concentration CDNC, ice crystal number concentration ICNC, cloud ice mass $x_i$ and cloud water mass $x_l$). Rain and snow are diagnostic variables. This implies that sedimentation happens within one time step (precipitation is removed immediately taking into account evaporation and sublimation is allowed to take place). The legitimation for doing so is the high fall speed of rain and snow.

ECHAM6-HAM2 can be run in free or nudged mode (Zhang et al., 2012). For the latter prognostic variables of ECHAM6 are assimilated to measurement based reference data, e.g. ERA INTERIM (Dee et al., 2011).

### 5.2 Aerosol particle scheme

Aerosol particles in ECHAM6-HAM2 are divided into four log-normal size modes: nucleation mode (median radius smaller than 0.005 $\mu$m), Aitken mode (median radius between 0.005 $\mu$m and 0.05 $\mu$m), accumulation mode (median radius between 0.05 $\mu$m and 0.5 $\mu$m) and coarse mode (median radius larger than 0.5 $\mu$m). Additionally, particles are distinguished by solubility, so that the total aerosol population can be captured by seven modes (M7), which are shown in Fig. 5.1. Sesartic et al. (2012) added bacteria to the aerosol species of the original setup, so that M7 can be extended to eight modes (M8). This extension is not used in this thesis.

Aerosol compounds which are included are sulfate (SU), black carbon (BC), particulate organic
matter (POM), sea salt (SS) and mineral dust (DU).

Within the soluble modes each aerosol particle is a composition of different aerosol compounds (internally mixed). The different aerosol modes are externally mixed, so that each mode is represented separately (Zhang et al., 2012). All aerosol modes are interactive, which means that aerosol mass and number can be transferred between the modes. That enables to describe the mixing state of aerosol particles. The number and compound masses for each log-normal mode are prognostic variables. The standard deviation of the log-normal modes is assumed to be constant.

Aerosol particles are either emitted directly into the atmosphere or formed within the atmosphere by nucleation (nucleation mode particles). Dust and sea salt particles are emitted online by interactive schemes based on meteorological conditions, e.g. wind speed. Black/organic carbon is emitted offline by using an emission database. While sea salt is directly emitted into the soluble mode due to its high hygroscopicity, dust and black/organic carbon are emitted insoluble assuming that they are not hygroscopic directly after emission.

Aerosol particles are removed from the atmosphere by sedimentation (dry deposition) or different wet scavenging pathways (wet deposition). The scavenging pathways are impaction-scavenging, where the particles are removed by collision with hydrometeors (cloud droplets, raindrops or snow flakes), and activation or nucleation scavenging, where the particles act as CCN or IN and thus are incorporated in a cloud droplet or ice-crystal.

During their lifetime in the atmosphere the different aerosol particles/modes can interact with each other and evolve over time. The two crucial processes for altering an aerosol mode and interaction of the aerosol modes within each other are coagulation and condensation.

Condensation of water and sulfate on aerosol particles lead to a growth of particles and/or can lead to a transfer of insoluble particles to soluble modes. Water uptake of the soluble modes is described based on the relative humidity and increases the equilibrium wet radius of the corresponding mode. The internally mixed amount of black/organic carbon does not influence the water uptake. Insoluble modes are not able to take up water because they are not hygroscopic. However, if enough soluble material is taken up by an insoluble particle, the insoluble particle gets hygroscopic. This is also called aging of the aerosol particle. This process can happen due to condensation of sulfuric acid or due to coagulation of the insoluble mode with a soluble component, e.g. sulfate. The condensation of sulfuric acid is limited by the availability and the diffusion to the surface of the insoluble particles. Moreover, there is a competition between nucleation and condensation.

Coagulation can happen within one mode (intra-modal coagulation) and between different modes (inter-modal coagulation). Intra-modal coagulation decreases the number of aerosol particles within one mode and increases the average particle mass within this mode because the total mass does not change. Between dust particles the intra-modal coagulation is neglected because
the sticking coefficient (describing how likely two aerosol particles stick together after collision) is to small. Inter-modal coagulation leads to a transfer of the average dry mass from one to another mode. The growing mode has a higher average mass after coagulation happened with the same amount of particles as before. The shrinking mode looses particles but has the same average mass per particle as before. Coagulation between insoluble and soluble modes can lead to aging of the particles (transfer to soluble modes). However, coagulation between a large insoluble and a small soluble particle may not lead to aging as in the case of coagulation between the nucleation mode and the insoluble Aitken or insoluble accumulation mode or coagulation between the soluble Aitken mode and the insoluble accumulation mode.

Both coagulation and condensation is calculated simplified for the average mode radius and not by integrating over the whole aerosol mode. Particles can grow larger than the upper limit of their aerosol mode. Therefore the particles are repartitioned between the modes at the end of the time step to avoid overlapping of different modes.

Figure 5.2 shows the processes influencing the aerosol dynamics in ECHAM6-HAM2.
Figure 5.2: Schematic of aerosol processes in ECHAM6-HAM2 based on Fig. 5.1 and Vignati et al. (2004).
5.3 Mixed-phase clouds and freezing parameterization schemes

Mixed-phase clouds and cirrus clouds are distinguished by temperature in ECHAM6-HAM2. Mixed-phase clouds form from supercooled cloud droplets when some droplets freeze. They can exist in the temperature range between 238.15 and 273.15 K. Below 238.15 K all cloud droplets are transformed to ice crystals. Due to the Wegener-Bergeron-Findeisen process, a mixed-phase cloud can fully glaciate (even above 238.15 K).

Possible IN for immersion freezing in ECHAM6-HAM2 are mineral dust and BC particles. Since the aerosol particles have to be immersed in cloud droplets, only dust and BC in the soluble modes are relevant. From a size perspective, accumulation and coarse mode are taken into account for mineral dust and Aitken, accumulation and coarse mode for BC.

The parameterization schemes used to describe the ice nucleation process are different for mixed-phase and cirrus clouds.

In the standard setup of ECHAM6-HAM2 heterogeneous freezing processes (immersion/condensation and contact freezing) in mixed-phase clouds are described by the lab-based parameterization scheme of Lohmann and Diehl (2006) [see chapter 2]. Other schemes which are implemented as part of this thesis are the CNT-based approach of Chen et al. (2008), the CNT-based approach using IMCA measurements (called IMCA CNT scheme), the lab-based approach of Niemand et al. (2012) and the field-based approach of DeMott et al. (2010) and DeMott et al. (2015). Not all of these schemes cover all possible IN species and most schemes focus on immersion freezing only.

5.4 Implementation of the immersion freezing schemes

The tendencies of the four prognostic variables for the two-moment cloud scheme (temperature, specific humidity, cloud water and cloud ice) are calculated in the subroutine cloud_cdnc_icnc, which is called every time step from the physics routine physc. The freezing parameterization schemes are part of this subroutine and can be chosen by changing the switch lhetfreez in the settingsfile: 1: Lohmann & Diehl scheme, 2: IMCA CNT scheme, 3: Niemand et al. scheme, 4: DeMott et al. scheme, 5: Chen et al. CNT scheme, 6: IMCA CNT scheme including a contact angle distribution (under development), 6: IMCA CNT scheme $\alpha(T)$ (under development).

All freezing schemes return a value for the mass freezing rate [kg/kg] (variable zfrzimm), which is then used to calculate the ice crystal number concentration [m$^{-3}$] (variable picnc) for all grid cells (1:kproma) on all levels (1:klev). The calculation is shown in the flowchart in Fig. 5.3.
Figure 5.3: Flowchart of the freezing parameterization schemes. Dark blue boxes show the input (round edges) and output of the calculation, light blue boxes the intermediate steps of the calculation. The variables used for the calculations are written right next to the arrow.
5.4 Implementation of the immersion freezing schemes

The following questions arose during the implementation of the new schemes:

1. **How to calculate the ice crystal number concentration from a nucleation rate?**

   For the Niemand et al. (2012) scheme and for the CNT based scheme the nucleation rate is transferred into a frozen fraction, which is multiplied by the number of activated aerosol particles to estimate the total number of particles that lead to a freezing event [m$^{-3}$]. To take into account that activated aerosol particles only freeze once the ice crystal number concentration of the former time step is subtracted (otherwise the model could freeze the same droplets several times).

   The number freezing rate is converted to a mass related freezing rate [kg/kg] by multiplication with the amount of liquid water inside the cloud [variable $z_{\text{xlb}(j1)}$] per cloud droplet number concentration [variable $z_{\text{cdnc}(j1,jk)}$].

   The mass related freezing rate is then summed up over all freezing modes and limited by the amount of liquid water inside the cloud to ensure that the mass freezing rate is not larger than the available liquid water. The resulting rate is converted back to a number freezing rate which is limited by the amount of cloud droplets inside the cloud ($z_{\text{cdnc}(j1,jk)}$). The value has to be higher than the minimum of cloud droplet number concentration [$z_{\text{cdnmin}(j1,jk)}$]. In a final step the cloud droplet number concentration and ice crystal number concentration is updated by subtracting the number freezing rate from the cloud droplet number concentration and adding it to the ice crystal number concentration.

2. **How to estimate the number of activated aerosol particles?**

   All freezing schemes, besides the one from DeMott et al. (2010), need the number of activated aerosol particles, or the fraction of aerosol particles which can act as an immersion IN, as an input parameter to calculate the freezing rate. This number is currently parameterized in ECHAM6-HAM2 using the Lin and Leaitch (1997) scheme. Alternatively the Abdul-Razzak and Ghan (2000) scheme could be used, which is currently only implemented in a beta-version. The Abdul-Razzak and Ghan (2000) scheme is more sophisticated than the Lin and Leaitch (1997) scheme because it takes the size and composition of the aerosol particles into account. It leads to more activated aerosol particles compared to the Lin and Leaitch (1997) scheme. However, it underpredicts CDNC if large particles are in competition with small ones.

   The best approach to keep track of the number of activated aerosol particles is to store them. This can be done by using a sophisticated aerosol processing scheme, e.g. Hoose et al. (2008), where the number of activated aerosol particles is “traced”. Using an aerosol processing scheme the problem of freezing the same droplets several times disappears.
Since the processing of aerosol particles is monitored it is not necessary to subtract the ice crystal number concentration of the former time step from the number freezing rate.

3 How to define the minimum of the cloud droplet number concentration (CDNC)?

Since the parameterization of particle activation is more uncertain than the saturation adjustment for cloud water it can happen that water vapor is condensing (due to the saturation adjustment) although the criterion of the activation parameterization is not full filled. Assuming that each cloud has a minimum CDNC, a minimum threshold for cloud droplets ($z_{cdn\text{min}}$) is introduced. This threshold is usually 40 droplets cm$^{-3}$. However, because there are hardly any atmospheric measurements of CDNC (especially in clean supercooled mixed-phase clouds), this value is arbitrary. In the simulations of this thesis the threshold was reduced to 10 droplets cm$^{-3}$ to ensure that the limit is not reached often. This happens more frequently in the single column model setup because less aerosol particles might be available to form cloud droplets. That is due to the missing transport of aerosol particles from the neighboring columns.

4 How to represent a time-dependent process?

The [Lohmann and Diehl (2006)] scheme and the CNT based scheme are time-dependent parameterization schemes. The standard resolution (T63 L31) uses a model time step of 12 minutes. 12 minutes is a rather long time period in the perspective of freezing and could lead to a overestimation of the freezing rate, in particular in the temperature regime where the frozen fraction is significantly below one.

If the time step is too large to represent the process correctly there are two possibilities to solve this issue: either to introduce a sub-time stepping or to limit the time step artificially. Sub-time stepping means that the time step is increased for a certain process aligned with the needs. If the process has interdependences with other processes the sub-time stepping has to be adapted for the other processes as well. That makes a realization of sub-time stepping for freezing difficult since e.g. the Wegener-Bergeron-Findeisen process is connected to the ice crystal number concentration and would need to be sub-time stepped as well. Using a fixed artificial time step would mean that the process is not calculated for the whole model time step but only for a timespan (smaller than the time step) which suits the process. For freezing this would for example mean that the freezing rate is calculated for the first ten seconds of the model time step only.

The methods used here are taking the model time step as usual or taking a fixed time step (different times are tested).

Using a CNT-based parameterization scheme with a contact angle distribution raises an additional question related to time. Since the most efficient aerosol particles, having the smallest $\alpha$, freeze first, the contact angle distribution changes with temperature/time. The
5.4 Implementation of the immersion freezing schemes

distribution is “eaten up” from the left to the right if there are no new aerosol particles
entering the cloud. Taking the same contact angle distribution every time step (indepen-
dent of the length of the time step) the most efficient contact angles are available over and
over again leading to an unrealistic representation of the freezing process. When using a
contact angle distribution the distribution has to change with time. Otherwise the freezing
process will be overestimated. The change of the contact angle distribution has not to be
accounted for when the aerosol particles are refilled within the time step.

Ervens and Feingold (2013) investigate the sensitivity of immersion freezing to time \( t \)
compared to \( T \), particle size \( (d_{IN}) \) and \( \alpha \) and find the lowest sensitivity with respect to
\( t \). In their case study they increase the time by three orders of magnitude to get the same
impact on the frozen fraction as from a temperature change of 1 K. That raises the question
how strong the temperature changes are from one time step to another in the model. To
evaluate this question four days of simulation with ECHAM6-HAM2 were done. The
temperature and the temperature tendency were written to the output after each time step.
The data is filtered for all mixed-phase cases resulting in 30-100 million values of \( \frac{dT}{dt} \).
Note that some mixed-phase clouds are counted several times in this simple analysis.
However, since the data volume is quite large, that should not disturb the analysis. The
values are plotted as a histogram in Fig. 5.4. It can be seen that it is difficult to make
a general statement about the temperature change in a mixed-phase cloud from one time
step to another. The histogram looks different when the temperature tendency instead of
the calculated temperature difference is used, which is due to the use of the TKE scheme
that enters the temperature tendency. Concentrating on the actual temperature difference
between two time steps [Fig. 5.4(b)], the temperature change is in approximately half of
the cases significant and in the other half not. Therefore the role of time compared to
temperature cannot be evaluated with this analysis. It might be better to investigate the
model results dependent on resolution (length of time step) instead as done in chapter 6.

Ervens and Feingold (2013) recommend to use time-independent CNT-based expressions
in large-scale models, dependent on \( T \), size and aerosol type. The case study in chap-
ter 6 gives an idea how time-dependent and time-independent CNT-based parameteriza-
tion schemes compare to each other. Besides, the sensitivity to model resolution and the
time step, is investigated in chapter 6 and different time-setsups are tested.

Large-scale versus small-scale temperature

There are two possible temperatures which can be used to calculate the freezing rate. The
temperature can either be calculated based on the small scale temperature tendency (see
2.2) or the current temperature can be used without any turbulence corrections. While the
Lohmann and Diehl (2006) scheme uses the temperature tendency including small scale
fluctuations all other schemes use the current temperature instead. The reason are inconsistencies found in the calculation of the small scale vertical velocity and problems with reproducing the temperature evolution in the model when using the temperature tendency including the small scale turbulences (for more details see the Bachelor thesis of Christian Zeman). Reasons might be problems with the Turbulent Kinetic Energy (TKE)-scheme.

![Histogram showing the temperature difference in a mixed-phase cloud from one time step to the next. Fig. (a) temperature tendency taking the turbulence into account multiplied with the time step, Fig. (b) difference of the temperature and the temperature the time step before.](image)

In the appendices A-E the commented source code of the different freezing schemes from the subroutine `cloud_cdnc_icnc.f90` (main coding part of the schemes) can be found. Additional changes/adaptations have been done in `mo_ham_streams.f90`, where the diagnostic output of HAM is defined and `mo_ham_m7_freezing.f90`, where the diagnostic output of HAM is set. The complete code related to this thesis can be found in the following development branch: [https://svn.iac.ethz.ch/external/echam-hammoz/echam6-hammoz/branches/luisa_ickes4](https://svn.iac.ethz.ch/external/echam-hammoz/echam6-hammoz/branches/luisa_ickes4)

Changes are implemented according to the ECHAM-HAMMOZ coding rules. The user abbreviation LI stands for Luisa Ickes and CZ for Christian Zeman, who implemented the [Niemand et al. (2012)](#) scheme as part of his Bachelor thesis.
5.5 The single column model setup

The single column model (SCM) is an one-dimensional setup where the model is run only over one grid point (see Fig. 5.5). It represents one grid cell of the global model with as many vertical levels as defined by the resolution. It is an ideal setup for testing new parameterizations because the behavior of the model physics can be analyzed isolated from the effects of large-scale dynamics. The output of the SCM is interpolated with time but not in the vertical dimension. Because the neighboring cells are missing (no horizontal dimension), the horizontal processes and tendencies are not calculated and the model physics remain unaffected by these. To describe the boundary conditions a forcing for the SCM is needed where temperature \( T \), horizontal wind \((u,v)\), specific humidity \( q \) and surface pressure \( p \) have to be defined. The first (time) step of the forcing file is the initial state of the SCM. From the initial state the SCM can run in three different modes: in a free mode, in a forced mode or in a nudged mode. In a free mode the SCM evolves freely from the initial state. In a forced mode the SCM state \((T,u,v,q)\) is overwritten at the beginning of each time step to force the column to a certain meteorology. In a nudged mode external tendencies from the forcing file can be used or added to the internal tendencies or the state of the SCM is relaxed to the forced state (variables will be restricted to a neighborhood of the given trajectory from the forcing file).

The functionality of the SCM makes it feasible to emulate situations which are of interest e.g. for testing parameterization schemes. When using the SCM to test microphysical processes an issue is that without advection aerosol particles cannot be transported into the grid cell. Depending on the position of the grid cell this means that no or too few aerosol particles exist in the SCM. In these cases the aerosol concentration and number needs to be prescribed.

Figure 5.5: Schematic sketch of a GCM and a single column. Figure courtesy Tim Ball.
5. A The Lohmann & Diehl scheme

The Lohmann & Diehl scheme requires a cooling rate. The cooling rate inside the cloud can be expressed with the (dry) adiabatic temperature gradient:

\[ \frac{dT}{dz} = -\frac{g}{c_p} \]

\[ \Rightarrow \frac{dT}{dt} = -\frac{g}{c_p} \cdot \frac{dz}{dt} = -\frac{g}{c_p} \cdot w. \]

Note that using the dry adiabatic temperature gradient is a simplification and using the wet adiabatic temperature gradient would be more realistic. The vertical velocity \( w \) has to be converted to the pressure velocity \( \omega \) since that is used in ECHAM6-HAM2. Starting from the hydrostatic equation yields:

\[ \frac{dp}{dz} = -\rho_{air} \cdot g \]

\[ \Rightarrow \frac{dp}{dz} \cdot \frac{dt}{dt} = -\rho_{air} \cdot g \]

\[ \Rightarrow \frac{dp}{dt} = \omega = -\rho \cdot g \cdot \frac{dz}{dt} = -\rho_{air} \cdot g \cdot w \]

\[ \Rightarrow w = -\frac{\omega}{\rho_{air} \cdot g} \]

The resulting adiabatic temperature gradient in pressure coordinates is the following:

\[ \frac{dT}{dt} = \frac{g}{c_p} \cdot w = -\frac{g}{c_p} \cdot \frac{\omega}{\rho_{air} \cdot g} = \frac{\omega}{c_p} \cdot \frac{1}{\rho_{air}}. \]

The vertical velocity \( \omega \) consists of a large-scale term (\( \omega_{\text{large scale}} \)) and a small scale term representing the turbulent fluctuations. The latter is not resolved in a GCM like ECHAM6-HAM because the resolution is too coarse. Therefore a turbulence parameterization scheme is used to estimate \( \omega \) based on the turbulent kinetic energy (TKE) [Lohmann et al. (1999)]:

\[ \omega = \omega_{\text{large scale}} - 1.33 \sqrt{\text{TKE}} \cdot \rho_{air} \cdot g. \]

The number freezing rate \( J_{\text{imm}}[\text{m}^{-3} \cdot \text{s}^{-1}] \) can be converted to a mass related freezing rate by multiplying with \( q_l \) ([\( q_l \]=kg kg\(^{-1}\)) and diving with CDNC ([CDNC]=m\(^{-3}\)). It is numerically integrated over time:

\[ J_{\text{imm}}[\text{kg} \cdot \text{kg}^{-1}] = q_l \cdot \left( 1 - \exp(-J_{\text{imm}}[\text{m}^{-3} \cdot \text{s}^{-1}] \cdot \frac{q_l}{\text{CDNC} \cdot \Delta t}) \right). \]
5.A The Lohmann & Diehl scheme

!case 1: Lohmann–Diehl parameterization scheme

!Calculation of the number of immersion IN for two different dust types and BC:

\[ znaimmdl = 32.3 \cdot dp \cdot \text{fracdusol}(j,l,jk) \quad \text{montmorillonite} \]
\[ znaimmdk = 6.15 \cdot 10^{-2} \cdot dp \cdot \text{fracdusol}(j,l,jk) \quad \text{kaolinite} \]

\[ znaimmbc = 2.91 \cdot 10^{-3} \cdot dp \cdot \text{fracbcsol}(j,l,jk) \]

!Calculation of the vertical velocity and corresponding temperature tendency:

\[ zomega = \frac{p \cdot \text{vervel}(j,l,jk) - 1.33 \cdot dp \cdot \text{SOBT}(ptikem1(j,l,jk)) \cdot \text{srho}(j,l,jk) \cdot g}{z \cdot \text{rho}(j,l,jk)} \]
\[ ztte = \frac{zomega}{cpd \cdot z \cdot \text{rho}(j,l,jk)} \]

!Calculation of the nucleation rate \([1/m^3/s]\):

\[ zfrzimm = -\left( znaimmdl + znaimmbc \right) \cdot \text{srho}(j,l,jk) \cdot \text{rho}_2o \cdot \text{EXP}(t_{melt} - z_{tmp}(j,l)) \cdot \text{MIN}(ztte, 0.1 \cdot dp) \]

!Calculation of the nucleation rate \([kg/kg]\): Time integration:

\[ zfrzimm = zxlb(j,l) \cdot \left( 1 - \exp\left(-zfrzimm \cdot zxlb(j,l) / zcdnc(j,l,jk) \cdot ztmst \right) \right) \]
5 ECHAM6-HAM2

5.B CNT based parameterization schemes

Four different types of CNT based parameterization schemes are implemented into ECHAM6-HAM2: the Chen et al. (2008) parameterization scheme for montmorillonite, kaolinite and soot particles (case 2a) and three different versions of the IMCA parameterization scheme based on CNT using parameters estimated from ZINC/IMCA measurements (see chapter 4) for kaolinite, illite, montmorillonite, microcline and ATD (case 2b-2d). The IMCA parameterization schemes distinguish by the contact angle scheme used (2b: single-\( \alpha \) fit \( \Delta g^\# \), 2c: \( \alpha(T) \), 2d: \( \alpha \)-pdf). The formulation of \( J_{\text{imm}} \) is slightly different between cases 2a and 2b (2c, 2d respectively). In case 2b the formulation of Reinhardt and Doye (2013) is used for the interfacial tension \( \sigma_{iw} \) and the prefactor does not take the Zeldovich factor into account (see chapter 4). The evaluation of the laboratory data for scheme 2b resulted in a value for the geometric term \( f \) (directly), in Chen et al. (2008) the contact angle was estimated and the geometric term calculated using Eq. 4.2.

In the scheme of Chen et al. (2008) an upper limit for the activated fraction is suggested to account for the limited validity of the stochastic assumption of the classical nucleation theory over the global model time step length (Hoose et al., 2010). In the case of mineral dust it is assumed that 100% of the particles activate so that there is no difference to the other CNT based approaches. In the case of soot the activated fraction is limited to 10%.

Scheme 2c and 2d are still under development.

Case 2a

```plaintext
! Implementation of Chen et al. CNT scheme

! Definition of constants:
  ah = 6.63E-34_dp ! (global constant) Planck

! Humidity variables:
  zt = ztp1tmp(jl) - 273.15_dp ! temperature in Celsius Tc
  zaw = 1._dp ! water activity (=1 on water saturation line)

! Saturation pressure over water (Tc):
  zpesw = 6.112E2_dp*EXP(17.62_dp*zt/(243.12_dp+zt))

! Saturation pressure over ice (Tc):
  zpesi = 6.112E2_dp*EXP(22.46_dp*zt/(272.62_dp+zt))

! Volume of a water molecule in ice (Tc):
  zvw = 2.99E-26_dp/(916.7_dp-0.175_dp*zt-5.4_dp*zt**2_dp)

! Interfacial tension between ice and water (Tc) following following Pruppacher and Klett 2000:
  zsigmaiw = 1.0E-3_dp*(28.0_dp+0.2_dp*zt)

! Estimation of the critical radius:
  zrgimm = MAX(2.0_dp*zvw*zsigmaiw/ak/ztp1tmp(jl)/LOG(zaw*zpesw/zpesi),zeps)
  ! max because: T >= 274 K (esi > esw -> log gets negative)

! Calculation of the geometric term f:
  zmbe = COS(40.17_dp*api/180.0_dp) ! cos of contact angle bc
```

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5. B CNT based parameterization schemes

\[ z_{\text{du}} = \cos(30.98 \_dp \ast \text{api}/180. \_dp) \]

\[ \text{!cos of contact angle du (mont)} \]

\[ z_{\text{frac2}} = \text{rdry(iaits)} \#ptr(jl,jk,krow)/zrgimm \]

\[ \text{!fraction radii for mode 2} \]

\[ z_{\text{frac3}} = \text{rdry(iaccs)} \#ptr(jl,jk,krow)/zrgimm \]

\[ \text{!fraction radii for mode 3} \]

\[ z_{\text{frac4}} = \text{rdry(icoas)} \#ptr(jl,jk,krow)/zrgimm \]

\[ \text{!fraction radii for mode 4} \]

\[ z_{\text{phibc2}} = \text{SORT}((1.\_dp-2.\_dp\_zmbc\_zfrac2+zfrac2**2)*bc, \text{mode 2}) \]

\[ z_{\text{phibc3}} = \text{SORT}((1.\_dp-2.\_dp\_zmbc\_zfrac3+zfrac3**2)*bc, \text{mode 3}) \]

\[ z_{\text{phibc4}} = \text{SORT}((1.\_dp-2.\_dp\_zmbc\_zfrac4+zfrac4**2)*bc, \text{mode 4}) \]

\[ z_{\text{phidu3}} = \text{SORT}((1.\_dp-2.\_dp\_zmdu\_zfrac3+zfrac3**2)*du, \text{mode 3}) \]

\[ z_{\text{phidu4}} = \text{SORT}((1.\_dp-2.\_dp\_zmdu\_zfrac4+zfrac4**2)*du, \text{mode 4}) \]

\[ \text{!Geometric term f:} \]

\[ z_{\text{bc2}} = 0.5 \_dp \ast (1.\_dp+((1-\_zmbc\_zfrac2)/zphibc2)**3+zfrac2**3(2-3*(zfrac2-zmbc)/zphibc2)**3)+3*\_zmbc\_zfrac2**2((zfrac2-zmbc)/zphibc2-1)) \]

\[ \text{!has to be between 0 and 1} \]

\[ z_{\text{bc2}} = \text{MAX}(z_{\text{bc2}}, \text{zeps}) \]

\[ z_{\text{bc2}} = \text{MIN}(z_{\text{bc2}}, 1.\_dp) \]

\[ \text{!here: MIN(MAX()) already included:} \]

\[ z_{\text{bc3}} = \text{MIN(MAX(zeps, 0.5 \_dp\ast (1.\_dp+(1-\_zmbc\_zfrac3)/zphibc3)**3+zfrac3**3(2-3*(zfrac3-zmbc)/zphibc3)**3)+3*\_zmbc\_zfrac3**2((zfrac3-zmbc)/zphibc3-1))), 1.\_dp) \]

\[ z_{\text{bc4}} = \text{MIN(MAX(zeps, 0.5 \_dp\ast (1.\_dp+(1-\_zmbc\_zfrac4)/zphibc4)**3+zfrac4**3(2-3*(zfrac4-zmbc)/zphibc4)**3)+3*\_zmbc\_zfrac4**2((zfrac4-zmbc)/zphibc4-1))), 1.\_dp) \]

\[ z_{\text{du3}} = \text{MIN(MAX(zeps, 0.5 \_dp\ast (1.\_dp+(1-\_zmdu\_zfrac3)/zphidu3)**3+zfrac3**3(2-3*(zfrac3-zmdu)/zphidu3)**3)+3*\_zmdu\_zfrac3**2((zfrac3-zmdu)/zphidu3-1))), 1.\_dp) \]

\[ z_{\text{du4}} = \text{MIN(MAX(zeps, 0.5 \_dp\ast (1.\_dp+(1-\_zmdu\_zfrac4)/zphidu4)**3+zfrac4**3(2-3*(zfrac4-zmdu)/zphidu4)**3)+3*\_zmdu\_zfrac4**2((zfrac4-zmdu)/zphidu4-1))), 1.\_dp) \]

\[ \text{!Activation energy deltag#:} \]

\[ z_{\text{deltagbc}} = 14.4E-20 \_dp \]

\[ z_{\text{deltagdu}} = 15.7E-20 \_dp \]

\[ \text{!Energy barrier:} \]

\[ z_{\text{deltagst}} = 4. \_dp \ast \text{api}/3. \_dp\_zsizmaiwa\_zrgimm**2 \]

\[ \text{!homogeneous delta g} \]

\[ \text{!Calculation of freezing rate:} \]

\[ \text{!formula (CNT): Jimm=zrgimm\_Aimm\_N**2*sqrt(f)*exp((-deltag-\_f\_deltagst)/kT)} \]

\[ \text{!ambient prefactor:} \]

\[ \text{Aimm = 1. E19. \_dp\_ak**3. \_dp\_zpltmp(jl)**3. \_dp\_LOG(zaw\_zpesw\_zpesis)**2. \_dp\_4. \_dp/ah/zxw/zsizmaiwa**2 \& \_SQR4(4\_zasizmaiwa/ak/zpltmp(jl))} \]

\[ \text{!Nucleation rate for each species and each mode:} \]

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zfrzimmdu3 = zAimm*rdry(iaccs)ptr(jl,jk,krow)**2*SQRT(zfdu3)*EXP((-zdeltau-dzfdu3+zdeltagst)/ak/ztp1tmp(jl))

zfrzimmdu4 = zAimm*rdry(icoas)ptr(jl,jk,krow)**2*SQRT(zfdu4)*EXP((-zdeltau-dzfdu4+zdeltagst)/ak/ztp1tmp(jl))

zfrzimmbc2 = zAimm*rdry(iaits)ptr(jl,jk,krow)**2*SQRT(zfbc2)*EXP((-zdeltagbc-zfbc2+zdeltagst)/ak/ztp1tmp(jl))

zfrzimmbc3 = zAimm*rdry(iaacss)ptr(jl,jk,krow)**2*SQRT(zfbc3)*EXP((-zdeltagbc-zfbc3+zdeltagst)/ak/ztp1tmp(jl))

zfrzimmdu4 = zAimm*rdry(icoas)ptr(jl,jk,krow)**2*SQRT(zfdu4)*EXP((-zdeltau-dzfdu4*zdeltagst)/ak/ztp1tmp(jl))

! Summed up freezing rate [1/s] for one type:
! dust:
zfrzimmdu = zfrzimmdu3 + zfrzimmdu4

! BC:
zfrzimmbc = zfrzimmbc2 + zfrzimmbc3 + zfrzimmbc4

! activated fraction (limitation of freezing):
zfracd = 1._dp
zfracbc = 0.01_dp

! Number of frozen activated droplets [1/m^3] (time integration):
zfrzimm = MIN(zfracd*ndusol_strat(jl,jk,jrow)+zfracbc*nbcsol_strat(jl,jk,jrow)), &
zfracd*ndusol_strat(jl,jk,jrow)+(1._dp-EXP(-zfrzimmdu*ztmst))+
zfracbc*nbcsol_strat(jl,jk,jrow) &
*(1._dp-EXP(-zfrzimmbc*ztmst))

! Pseudorate: subtracting frozen droplets from last time step:
zfrzimm = MAX(zfrzimm - picnc(jl,jk), 0._dp)

! Conversion to mass nucleation rate [kg/kg]:
zfrzimm = zxlb(jl)/(zcdnc(jl,jk)*zeps) * zfrzimm

!<<LI

---

**Case 2b**

!>>LI [implementation of IMCA CNT scheme: single-alpha + fit delta#]

! Definition of constants:
ah = 6.63E-34_dp !(global constant) Planck

! humidity variables:
zt = ztp1tmp(jl)-273.15_dp !temperature in Celsius Tc
zaw = 1._dp !water activity (=1 on water saturation line)

! saturation pressure over water (Tc):
zpesw = 6.112E2_dp*EXP(17.62_dp*zt/(243.12_dp+zt))

! saturation pressure over ice (Tc):
zpesi = 6.112E2_dp*EXP(22.46_dp*zt/(272.62_dp+zt))

! volume of a water molecule in ice (Tc):
zvw = 2.99E-26_dp/(916.7_dp-0.175_dp*zt-5.E-6_dp*zt**2._dp)

! interfacial tension between ice and water following Reinhardt & Doye 2013 (Tc):
!sigmaiw0 = extrapolated value for monatomic water = 29.967
zsigmaiw = 1.E-3_dp*(29.967_dp + 0.18_dp*zt)
5.B CNT based parameterization schemes

! Estimation of the critical radius:
\[ \text{r}_{\text{critical}} = \text{MAX}(2. \times \text{zvw} \times \text{zsigmaiw}/\text{ak}/\text{ztpltmp}(\text{jl})/\text{LOG}(\text{zaw}+\text{zpesw}/\text{zpesi}), 274 \times \text{zvp}) \]

! max because: \( T > 274 \times \text{K} \) (esi > esw -> log gets negative)

! Geometric term \( f \) from fits (Ickes et al. 2015):
\[ \text{zfdu} = 0.2887298 \times \text{dp} + 0.29 \times \text{kd} \times \text{kaolinite} \]
\[ \text{zfdu} = 0.3626928 \times \text{dp} + 0.36 \times \text{kd} \times \text{illite} \]
\[ \text{zfdu} = 0.27785 \times \text{dp} + 0.28 \times \text{kd} \times \text{montmorillonite} \]
\[ \text{zfdu} = 0.1051368 \times \text{dp} + 0.11 \times \text{kd} \times \text{microcline} \]
\[ \text{zfdu} = 0.1430357 \times \text{dp} + 0.14 \times \text{kd} \times \text{ATD} \]

! Activation energy \( \delta g \) from fits:
\[ \text{zdeltagd} = 9.9517142 - 20 \times \text{dp} \times \text{kd} \times \text{kaolinite} \]
\[ \text{zdeltagd} = 8.9330281 - 20 \times \text{dp} \times \text{kd} \times \text{illite} \]
\[ \text{zdeltagd} = 10.03439 - 20 \times \text{dp} \times \text{kd} \times \text{montmorillonite} \]
\[ \text{zdeltagd} = 11.9732931 - 20 \times \text{dp} \times \text{kd} \times \text{microcline} \]
\[ \text{zdeltagd} = 12.5767935 - 20 \times \text{dp} \times \text{kd} \times \text{ATD} \]

! Energy barrier of nucleation:
\[ \text{zdeltagst} = 16. \times \text{dp} \times \text{api}/3 \times \text{dp} \times \text{zv} \times \text{zsigmaiw} \times \text{ak} \times \text{ztpltmp}(\text{jl}) \times \text{LOG}(\text{zaw}+\text{zpesw}/\text{zpesi}) \]

! Calculation of freezing rate

! formula (CNT): \( \text{jimm} = \text{zfzimm} \times \text{Cprefac} \times \exp((-\text{zdeltagd} - f \times \text{zdeltagst})/kT) \)

! Cprefac = \( ns \times kT/h \)

! Prefactor:
\[ \text{zp prefac} = 1. \times 10^9 \times \text{dp} \times \text{zpltmp}(\text{jl})/\text{ah} \]

! Nucleation rate \([/s/m^2]\):
\[ \text{zfzimm} = \text{zp prefac} \times \exp((-\text{zdeltagd} - \text{zfdu} \times \text{zdeltagst})/\text{ak} \times \text{ztpltmp}(\text{jl})) \]

! Nucleation rate \([/s]\):
\[ \text{zfzimmdu3} = \text{zfzimmdu} \times 4 \times \text{dp} \times \text{api} \times \text{rdry}(\text{iaccs}) \times \text{ptr}(\text{jl}, \text{jk}, \text{krow}) \times \text{rdry}(\text{iaccs}) \times \text{ptr}(\text{jl}, \text{jk}, \text{krow}) \]
\[ \text{zfzimmdu4} = \text{zfzimmdu} \times 4 \times \text{dp} \times \text{api} \times \text{rdry}(\text{icoas}) \times \text{ptr}(\text{jl}, \text{jk}, \text{krow}) \times \text{rdry}(\text{icoas}) \times \text{ptr}(\text{jl}, \text{jk}, \text{krow}) \]
\[ \text{zfzimmdu} = \text{zfzimmdu3} + \text{zfzimmdu4} \]

! Frozen fraction (time integration):
\[ \text{zfzimmdu3} = 1. \times \text{dp} \times \exp(-\text{zfzimmdu3} \times \text{ztmsl}) \]
\[ \text{zfzimmdu4} = 1. \times \text{dp} \times \exp(-\text{zfzimmdu4} \times \text{ztmsl}) \]

! Activated fraction (limitation of freezing):
\[ \text{zfzimmdu} = \text{zfzimmdu3} + \text{zfzimmdu4} \]

! Number of frozen activated droplets \([/m^3]\):
\[ \text{zfzimmdu3} = \min(\text{ndusol stratal} \times \text{tal} \times \text{zfzimmdu} \times \text{zfzimmdu3}) \]
\[ \text{zfzimmdu4} = \min(\text{ndusol stratal} \times \text{tal} \times \text{zfzimmdu} \times \text{zfzimmdu4}) \]
\[ \text{zfzimm} = \text{zfzimmdu3} + \text{zfzimmdu4} \]

! Pseudo rate: subtracting frozen droplets from last time step:
\[ \text{zfzimm} = \text{MAX}(\text{zfzimm} - \text{picn}(\text{jl}, \text{jk}), 0 \times \text{dp}) \]
! Mass nucleation rate [kg/kg]:

\[ \text{zfrzimm} = \frac{zxl{\text{"b}}(j{l})}{(zcdnc(j{l},jk)+zeps)} \times \text{zfrzimm} \]
5.C The Niemand et al. scheme

!>>CZ [implementation of ns parameterization scheme based on Niemand et. al. 2012]; LI [added numbers for different dust types]

! calculate n_s (density of ice-active surface sites) based on temperature:
!Niemand et al. 2012 original values for dust
za = −0.517_dp
zb = +8.934_dp
!†Ickes et al. 2015 derived values for different dust types:
!kaolinite:
! za = 0.9190762_dp
! zb = −3.7699987_dp
!illite:
! za = 1.09648_dp
! zb = −10.34858_dp
!montmorillonite:
! za = 0.9144647_dp
! zb = −2.7062854_dp
!microcline:
! za = 0.7275858_dp
! zb = 9.6348970_dp
!ATD:
! za = 0.3696394_dp
! zb = 16.0440291_dp

zdensiass = EXP(−za*(ztp1tmp(jl)−273.15_dp)+zb)

! Mean surface of one particle for the different modes approximated
! S = exp(2(ln sigma)^2) * pi * (2r)^2
! exp(2(ln sigma)^2) = conversion factor from mean to median of the size mode
!acc mode
zp_surfaces = 1.53741_dp * 4._dp * api * rdry(iaces)%ptr(jl,jk,krow) * rdry(iaces)%ptr(jl,jk,krow)
!coarse mode
zp_surfaces = 2.61406_dp * 4._dp * api * rdry(icoas)%ptr(jl,jk,krow) * rdry(icoas)%ptr(jl,jk,krow)

! Number of dust aerosols that are immersed in a droplet for different modes
znaimmdaus = ndusol_strat_a(jl,jk,jrow)
znaimmducs = ndusol_strat_c(jl,jk,jrow)

! Ice crystal number concentration difference for the different modes [1/m3]
! J = N_a,imm * FF(ns,S)
ziencdas = znaimmdaus * (1−EXP(−zp_surfaces*zdensiass))
ziencdcas = znaimmducs * (1−EXP(−zp_surfaces*zdensiass))

! Immersion freezing rate in [kg/kg]; subtraction of already frozen activated droplets
zfrzimm = MAX(ziencdas+ziencdcas−picnc(jl,jk),0._dp)
zfrzimm = zfrzimm*zxl_b(jl)/(zcnc(jl,jk)+zeps)
<<CZ
Two different versions of the field-based DeMott et al. parameterization are implemented: the version from 2010 and the dust-specific version from 2015. The dust-specific version is still under development. At the current status it can be seen as a upper limit for possible freezing of dust particles. It uses the number of all aerosol particles with a diameter larger 0.5 \( \mu \text{m} \) without any distinction in species, which means that it is assumed that all particles above the size limit are dust particles. The reason for this simplification is the structure of the aerosol particle scheme HAM. It is difficult to know how many particles above the size threshold are dust particles within the internally mixed modes.

```
!>>LI [DeMott et al. 2010 parameterization scheme transferred from Ulrik e branch.
!DeMott et al. 2010:
particles acting as IN initiate freezing:
! za = 0.00006594_dp
! zb = 3.33_dp
! zc = 0.0264_dp
! zd = 0.0033_dp
! zpot = zc*(273.16_dp-ztp1tmp(jl))+zd
! na_in: all particles above 0.5 mm (aerosol particle diameter)
! na_in*1.e-6_dp to convert from 1/m3 to 1/cm3
! prefactor 1.e-3 to convert from 1/l to 1/m3
! znaimm = 1.e-3_dp*(za*(273.16_dp-ztp1tmp(jl))**zb*na_in(jl,jk,jrow)*1.e-6_dp)**zpot
! Subtracting previously frozen particles, limit by znaimm:
! zfrrimm = MIN(znaimm, na_in(jl,jk,jrow) - picnc(jl,jk))
! Convert to mass freezing rate [kg/kg]:
! zfrrimm = zfrrimm*zxlb(jl)/(zcdnc(jl,jk)+zeps)

!DeMott et al. 2015: only mineral dust:
zb = 1.25_dp
zc = 0.46_dp
zd = -11.6_dp

! upper estimate using na_in similar to DeMott et al. 2010:
! be careful that is not a specific number for dust aerosol particles!
! na_in*1.e-6_dp to convert from 1/m3 to 1/cm3
! prefactor 1e-3 to convert from 1/l to 1/m3
! znaimm = 1.e-3_dp*(na_in(jl,jk,jrow)*1.e-6_dp)**zb*exp(zc*(273.16_dp-ztp1tmp(jl))+zd)
! Subtracting previously frozen particles, limit by znaimm:
! zfrrimm = MIN(znaimm, na_in(jl,jk,jrow) - picnc(jl,jk))
! zfrrimm = zfrrimm*zxlb(jl)/(zcdnc(jl,jk)+zeps)
! Convert to mass freezing rate [kg/kg]:
!zfrrimm = zfrrimm*zxlb(jl)/(zcdnc(jl,jk)+zeps)
<<LI```

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5.E Calculation of the ice crystal number concentration from a freezing rate

! Calculate freezing rate \([\text{kg/kg}]\): contact + immersion freezing:
\[ \text{ztmp1}_{1d}(j_l) = \text{zfrcnt} + \text{zfzimm} \]

! Limitation to liquid water (cannot be higher than liquid water):
\[ \text{ztmp1}_{1d}(j_l) = \text{MAX}(0.0_{dp}, \text{MIN}(\text{ztmp1}_{1d}(j_l), \text{zxl1b}(j_l))) \] !SF zfzl surrogate

! Calculate freezing rate \([1/m^3]\):
\[ \text{czfrz} = \text{cdnc} \times \text{frzr/}(\text{cloud liquid water} + \text{eps}) \]
\[ \text{ztmp2}_{1d}(j_l) = \text{zcdnc}(j_l, j_k) \times \text{ztmp1}_{1d}(j_l)/(\text{zxl1b}(j_l) + \text{eps}) \]
\[ \text{ztmp2}_{1d}(j_l) = \text{MAX}(\text{ztmp2}_{1d}(j_l), 0_{dp}) \] !SF zfzl surrogate

ENDDO !SF end loop j_l

! Set heterogeneous or homogeneous \((T<238 K)\) freezing rate \([\text{kg/kg}]\):
\[ \text{zfz}(1:kprom, j_k) = \text{MERGE}(\text{ztmp1}_{1d}(1:kprom), \text{zfz}(1:kprom, j_k), \text{lo}_{1d}(1:kprom)) \]

! Set heterogeneous or homogeneous \((T<238 K)\) freezing rate \([1/m^3]\):
\[ !\text{frzr} [1/m^3] \text{ must be} < \text{cdnc} - \text{cdnmin} \text{ and} > 0 \]
\[ \text{ztmp1}_{1d}(1:kprom) = \text{MIN}(\text{ztmp2}_{1d}(1:kprom), \text{zcdnc}(1:kprom, j_k) - \text{cdnmin}) \]
\[ \text{ztmp1}_{1d}(1:kprom) = \text{MAX}(\text{ztmp1}_{1d}(1:kprom), 0_{dp}) \]
\[ \text{zfzl}_{1d}(1:kprom) = \text{MERGE}(\text{ztmp1}_{1d}(1:kprom), \text{zfzl}_{1d}(1:kprom), \text{lo}_{1d}(1:kprom)) \]

! Estimate new cdnc after heterogeneous/homogeneous freezing \([1/m^3]\):
\[ \text{ztmp1}_{1d}(1:kprom) = \text{zcdnc}(1:kprom, j_k) - \text{zfzl}_{1d}(1:kprom) \]
\[ \text{ztmp1}_{1d}(1:kprom) = \text{MAX}(\text{ztmp1}_{1d}(1:kprom), \text{cqtmin}) \]
\[ \text{zcdnc}(1:kprom, j_k) = \text{MERGE}(\text{ztmp1}_{1d}(1:kprom), \text{zcdnc}(1:kprom, j_k), \text{lo}_{1d}(1:kprom)) \]

! Estimate new icnc \([1/m^3]\):
\[ \text{ztmp1}_{1d}(1:kprom) = \text{picnc}(1:kprom, j_k) + \text{zfzl}_{1d}(1:kprom) \]
\[ \text{ztmp1}_{1d}(1:kprom) = \text{MAX}(\text{ztmp1}_{1d}(1:kprom), \text{cqtmin}) \]
\[ \text{picnc}(1:kprom, j_k) = \text{MERGE}(\text{ztmp1}_{1d}(1:kprom), \text{picnc}(1:kprom, j_k), \text{lo}_{1d}(1:kprom)) \]
Arctic case study: testing the parameterization scheme

Mixed-phase clouds are the dominant cloud type in the Arctic and very sensitive to freezing parameterization schemes. Therefore the Arctic is a suitable region for testing freezing parameterization schemes. The SCM setup of ECHAM6-HAM2 is used in this chapter to test four different parameterization schemes in the framework of an Arctic case study.
6.1 The role of ice nucleation in Arctic clouds

Clouds play an important role in Arctic climate, its seasonality and feedback processes (Prenni et al., 2007). The dominant cloud type in the Arctic are low-level boundary clouds, which are mostly mixed-phase clouds (Prenni et al., 2007). During the Arctic field campaigns SHEBA and FIRE-ACE mixed-phase clouds were observed frequently in all seasons but summer. Arctic mixed-phase clouds can be found at temperatures as low as 242 K and persisting over long time periods of several hours up to several days. The cloud tops can be liquid on top with ice precipitation falling from this liquid cloud top (Verlinde et al., 2007). The phase of Arctic clouds is important for the radiation balance and has a profound impact on the lifetime of these clouds. The amount of liquid and ice water content of Arctic mixed-phase clouds is influenced by heterogeneous ice nucleation, cloud-scale dynamics, sea ice coverage and sea ice thickness (Prenni et al., 2007). It is assumed that heterogeneous ice nucleation, which is responsible for the initial ice formation in the cloud, is the main actor determining the longevity of Arctic mixed-phase clouds. Therefore the stability of these clouds is dependent on the IN concentration (Harrington et al., 1999). Already small changes in the IN concentration can change the structure of the mixed-phase cloud fundamentally (Harrington et al., 1999; Jiang et al., 2000) due to an active Wegener-Bergeron-Findeisen process. While the absence of IN can increase the life time of a mixed-phase clouds, IN can lead to glaciation and rapid ice precipitation that dries the cloud layer (Prenni et al., 2007). An increase in IN concentration by a factor of two to three can lead to a conversion of a largely liquid mixed-phase cloud deck to optically thin clouds (Prenni et al., 2007).

Typical IN types in the Arctic can be transported dust particles mainly from Asia (Barrie and Barrie, 1990; Pacyna and Ottar, 1989), transported pollution aerosol particles from anthropogenic sources (Barrie, 1986; Kerr, 1979; Shaw, 1982), transported aerosol particles from biomass burning (Frossard et al., 2011; Hegg et al., 2009; Iziomon et al., 2006; Sharma et al., 2013; Warneke et al., 2009, 2010) and aerosol particles from oceanic sources. The type of available aerosol particles and concentration varies considerably between seasons (Barrie, 1986; Quinn et al., 2002, 2009; Shaw, 1982).

The interaction of IN with Arctic mixed-phase clouds is not very well represented in many global models, which causes uncertainties in estimating the radiation balance and thus the sea ice coverage (Morrison et al., 2005). This inability of the models could be related to inadequate parameterizations of ice nucleation (Prenni et al., 2007). Modeled IN concentrations are dependent on the freezing parameterization scheme used and the treatment of IN depletion due to ice crystal nucleation and precipitation removal (Morrison et al., 2005; Prenni et al., 2007). Most models do not explicitly account for IN depletion and many parameterization schemes lead to rapid glaciation of clouds due to overestimation of the ice initiation and the Wegener-Bergeron-Findeisen process. Field based parameterization schemes are often based on measurements in the mid-latitudes and have therefore problems reproducing the freezing processes in the Arctic,
6.2 M-PACE case study: Setup

e.g. the Meyers scheme \cite{Prenni2007}. If the conversion from mixed-phase to ice clouds is overestimated, feedbacks, especially aerosol-cloud feedbacks, are not reproduced correctly. To correctly describe Arctic clouds, more specific the correct phase state of the clouds and thus the correct radiative impact, a model has to predict the number of IN, the in-cloud processing and their removal \cite{Prenni2007}.

The Atmospheric Radiation Measurement (ARM) Mixed-Phase Arctic Cloud Experiment (M-PACE; \cite{Klein2009}) is used as a case study to test different immersion freezing parameterization schemes introduced before. Furthermore, sensitivities of the parameterization schemes to different input parameters are investigated, such as estimated thermodynamic and kinetic parameters for the CNT-based schemes. The M-PACE campaign took place at the Northern slope of Alaska (close to Barrow, see Fig. 6.1) at the end of fall in 2004 (27.09.-22.10.2004). This case is a rather clean case with low droplet concentrations (between 10 and 100 particles cm\(^{-3}\)) and low IN concentrations (average below 0.001 particles cm\(^{-3}\)), which were measured with a CFDC \cite{Verlinde2007}. The liquid water content (LWC) was between 0.1 and 1 g m\(^{-3}\). Liquid cloud water was measured down to a temperature of 243.15 K. The aim of the campaign was to quantify the question if persisting liquid clouds are due to dynamics or microphysics. A SCM model intercomparison focused on two different cloud systems: a single-layer boundary layer stratocumulus deck (09.-11.10.2004) and a complicated multilayer stratus case (06.10.2004). The study showed that small changes in the synoptics can change the cloud microphysics considerably, which might be associated with the change of aerosol particle sources within the transported air mass due to different source regions or local pollution.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.1.png}
\caption{Domain and typical cloud situation of the M-PACE campaign [left: \cite{Klein2009}; right: \cite{Verlinde2007}].}
\end{figure}
The simulations shown in this chapter were done with the ECHAM6-HAM2 SCM for the time period 05.10.-22.10.2004. A vertical resolution of 31 levels was used, since the middle atmosphere is not of interest for this study. The initial state for the SCM is given by the ARM SCM forcing file (ARM [2006]), as well as the data needed to run the SCM in the nudged mode. Concerning the nudging the divergence is used from the forcing file. The variables $q$ and $T$ are nudged each time step to the reanalysis data with a relaxation time of 3 h. The model time step is 15 minutes. This approach was chosen to ensure that the SCM runs very close to the observations and the parameterization schemes can be tested under nearly similar meteorological conditions, which reduces differences due to the internal variability of the model. The aerosol concentrations are prescribed based on measurements of the Hand-Held Particle Counter HHPC-6: 72.2 particles cm$^{-3}$, 1.8 particles cm$^{-3}$ are in the coarse mode. The mass of the particles is defined as $5 \cdot 10^{-12}$ kg m$^{-3}$ for particles of the accumulation mode and $6.5 \cdot 10^{-9}$ kg m$^{-3}$ for particles of the coarse mode.

To make the case study more suitable for testing immersion freezing parameterization schemes of mineral dust, three changes are made to the original setup: first, it is defined that all aerosol particles are dust particles, second, the temperature is decreased by 10 K because otherwise the freezing events are not very distinct in the simulation, third, immersion freezing is the only heterogeneous freezing mode allowed to happen. The dust particles are directly “emitted” into the soluble mode because the dust is in general aged during the transport to the Arctic. However, this adaptations hinder a comparison to campaign data.

**Overview of the case study**

The original and adapted temperature and the humidity profile and time evolution of these variables is shown in Fig. 6.2. The black line is the 238.15 K isotherm to mark the region where immersion freezing can take place. The modeled ice and liquid water content is shown in Fig. 6.3 as a two-dimensional-profile and vertically integrated over the column in Fig. 6.4 (using the IMCA CNT scheme). It can be seen that between October 10th and 15th (day 5 to 10 of the campaign) the meteorological conditions are favorable for freezing to take place, which triggers the occurrence of mixed-phase clouds in this time period. They seem to be strongly related to temperature, as their structure follows the temperature profile. The ice phase on the other days below the 238.15 K isotherm is nearly completely resulting from sedimentation of ice crystals from cirrus clouds above. Therefore, this specific time period is chosen for the subsequent analysis to compare the different freezing schemes and test sensitivities of the schemes. It seems that the vertical resolution is too low to reproduce the liquid water layer on top of the ice phase at the top of the clouds as it was observed during the campaign.
6.2 M-PACE case study: Setup

Figure 6.2: Humidity and temperature profiles of the M-PACE campaign. The height is given on the y-axis, the time on the x-axis (date). The black line is the 238.15 K isotherm.

Figure 6.3: Simulated cloud ice and liquid water during the M-PACE campaign.
6.3 Sensitivity of the parameterization scheme

After the implementation of the new parameterization schemes, the sensitivity to the microphysical properties of the IN (such as the contact angle $\alpha$), to different mineralogical composition of the IN and to model resolution of the IMCA CNT scheme is tested in the framework of M-PACE including the adaptations mentioned above:

1. Model resolution and time step

It is tested how the results change with different model resolutions and different time steps. It is also investigated how using a fixed time step changes the outcome of the freezing parameterization compared to using the model time step (see chapter 5). In the SCM the resolution can only be changed in the vertical (no horizontal dimension) by changing the vertical resolution (= number of levels). Unfortunately only two setups are available at the moment: 31 levels or 47 levels including the middle atmosphere. Because the change of both setups is mainly in the upper troposphere and stratosphere the choice of 31 or 47 levels does not affect the results of the case study.

The standard time step of ECHAM6-HAM2 is 900 s. As an alternative the simulation can be run with a time step of 600 s. However, the time step cannot be further reduced with the current setup. Since 600 s is still quite a large time step the results are hardly affected by changing the time step accordingly. However, using a fixed time step of 10 s instead of the model time step to calculate the freezing rate changes the resulting ice content of the cloud. Comparing the vertical integrated numbers for the time period where immersion
freezing happens, leads to a decrease of approx. 60% in cloud ice (kg m\(^{-2}\)) when a fixed time step is used instead of the model time step. The issue should be further investigated with different resolutions and different time steps.

Different types of mineral dust acting as IN (different microphysical properties)

It is investigated how the freezing process changes when using different mineral dust types. This is realized by changing the microphysical properties of the IN expressed by the fit parameters from the laboratory measurements (see fit parameter in chapter 4 and within the implementation section of chapter 5). The results are shown in Fig. 6.5.

![Figure 6.5: Liquid water and ice simulated by the IMCA CNT scheme for different mineral dust composition.](image)
The freezing behavior of the different parameterization schemes changes considerably depending on the mineralogical composition of the IN. The amount of cloud ice produced reflects the efficiency of the mineral dust type used as IN. The most efficient IN, microcline (see chapter 4), produces the highest amount of cloud ice, the least amount is produced by illite. A decrease in cloud water immediately follows the increase of cloud ice. Comparing the results for montmorillonite and kaolinite shows that already small changes in the fit parameters \( \Delta(f) = 0.01 \) and \( \Delta(\Delta g^\#) = 0.08 \cdot 10^{-20} \) \( \text{J} \) lead to a different behavior in the model, at least in the case study investigated here.

Freezing peaks correlate with temperature changes. The different shapes of the curves for the different mineral dust types can be explained by their different freezing onset temperatures. Their freezing onset temperatures and medium freezing temperatures \( FF = 0.5 \) are shown in Fig. 6.6. The contour lines of certain frozen fractions follow different isotherms for the different mineral dust types.

To quantitatively compare the effect of different dust mineralogy on freezing, the fraction of cloud ice (IWP) of the sum of cloud ice and cloud water (LWP + IWP) is calculated by using the mean over the investigated time period for the vertically integrated variables \( \frac{\text{IWP}}{\text{LWP} + \text{IWP}} \). The numbers compare as follows: microcline has the highest fraction with 0.19, followed by ATD with 0.11. Montmorillonite yields a fraction of 0.04, kaolinite of 0.03 and illite of 0.02.

### 6.4 Comparison and behavior of the different parameterization schemes

In this section different immersion freezing parameterization schemes are compared. There are four different kind of schemes implemented in ECHAM6-HAM2: the Lohmann and Diehl (2006) laboratory based scheme, the Niemand et al. (2012) laboratory based scheme, the DeMott et al. (2010) field based scheme and the CNT based IMCA CNT scheme developed in this thesis. Figure 6.7 (upper panel) shows a comparison of the different schemes with regard to integrated cloud ice and cloud water. The differences are less pronounced than those resulting from different mineralogical compositions of the dust IN. To be able to better compare the different schemes the same particle mineralogical composition should be assumed. Otherwise the differences could be due to different mineralogical assumptions and not the scheme itself. Therefore the DeMott et al. (2010) scheme was replaced by its updated version (DeMott et al. 2015) and the Niemand et al. (2012) scheme by the fit of \( n_s(T) \) of the kaolinite data (chapter 4). Note that at the current state the DeMott et al. (2015) scheme only reflects an upper limit of freezing of dust. The comparison is shown in Fig. 6.7 (lower panel). Now, nearly all schemes produce the same amount of cloud ice except for the CNT based scheme. The reason could be a higher freezing onset temperature in the CNT case or a result of the time-dependence versus non-time-
dependence and an overestimation of the freezing rate due to that. Comparing Fig. 6.7 and Fig. 6.5, the illite curve with a lower freezing onset temperature would match the other parameterization schemes better. To investigate in more detail if the time-dependence lead to the difference, the simulation results when using a fixed time step of 10 s was additionally added to Fig. 6.7 (dashed line). The freezing curves still deviate from each other but the CNT scheme with a fixed time step compares better to the other schemes. This highlights the need of investigating the issue arising from large time steps and the possible necessity of sub-time stepping.
Figure 6.6: Frozen fraction contour lines simulated by the IMCA CNT scheme for different mineral dust composition. The color code is similar to Fig. 6.5 (dark blue=kaolinite, deepskyblue=montmorillonite, red=microcline, orange=ATD and dark magenta=illite). Temperature contour lines are also added to the Figure in black (solid=238.15 K, dashed=248.15 K, dotted=253.15 K, dot-dashed=258.15 K).
6.4 Comparison of the different parameterization schemes

Figure 6.7: Liquid water and ice simulated by different parameterization schemes.
Conclusions and outlook

The aim of this thesis was to develop a parameterization scheme for immersion freezing in mixed-phase clouds based on CNT and laboratory data, which can be used in a global climate model. The scheme was developed based on considerations about the unconstrained thermo-dynamic and kinetic parameters of CNT and on laboratory measurements of homogeneous and heterogeneous freezing (the latter from the ZINC/IMCA setup). The new IMCA CNT scheme was implemented into the ECHAM6-HAM2 GCM for five different mineral dust types. It was tested against three other parameterization schemes (two of which are empirical formulations from laboratory measurements, one of which is a scheme based on field measurements) in the context of the Arctic case study M-PACE.
Summary

1 CNT of homogeneous freezing: sensitivities to thermodynamic and kinetic parameters

The framework of CNT is not fully constrained since the properties of water are not completely understood yet. There are two unconstrained thermodynamic and kinetic parameters which influence the nucleation rate ($J_{\text{hom}}$) considerably: the interfacial tension between ice and water ($\sigma_{iw}$) and the activation energy describing the diffusion of a water molecule to the ice embryo ($\Delta g^\#$). Both cannot be measured directly for supercooled water. Therefore, many different formulations for $\sigma_{iw}(T)$ and $\Delta g^\#(T)$ exist based on different approaches to estimate these parameters. Depending on which formulation is used in the CNT framework to calculate $J_{\text{hom}}$, the results differ by many orders of magnitude. In this thesis, laboratory data of homogeneous freezing is used to constrain these two free parameters. A good combination to reproduce the freezing data is a $\sigma_{iw}(T)$ formulation from molecular models ([Reinhardt and Doye, 2013]) and a $\Delta g^\#(T)$ formulation derived from diffusion experiments of water ([Zobrist et al., 2007]). Due to the limitations of the analysis, it does not yield a final, comprehensive solution for the unconstrained parameters of CNT. Improved knowledge about the physics of supercooled water would also advance CNT.

2 CNT of immersion freezing: sensitivities to thermodynamic and kinetic parameters

Immersion freezing introduces one more unconstrained parameter into the CNT framework: the geometric term $f$ describing the microphysical properties of the IN. This term is usually estimated by fitting the free parameters of the CNT approach (including some assumptions about $f$) to laboratory data. An investigation of the sensitivity of the fitted $f$ to thermodynamic and kinetic parameters shows that the resulting value for $f$ strongly depends on the CNT framework, i.e. the pair of thermodynamic and kinetic parameters used. However, if the influence of the IN on the freezing process is described with at least two fit parameters, which are estimated by fitting to the data, the experimental freezing curves can be reproduced well independently of the formulation of the thermodynamic and kinetic parameters. The freedom given by the fitting compensates the uncertainty in thermodynamic and kinetic parameters. This means that the values of the fit parameters are not necessarily meaningful and cannot be compared easily if different CNT schemes were used.

3 Developing a CNT based parameterization scheme for ECHAM6-HAM2 using laboratory data
Emerging from the sensitivity studies, a procedure is developed to evaluate reasonable CNT schemes. It was used subsequently to determine two possible CNT schemes for the use in GCMs.

Following the analysis of homogeneous freezing data, $\sigma_{iw}(T)$ of Reinhardt and Doye (2013) and $\Delta g^#(T)$ of Zobrist et al. (2007) were also used (when not fitted) as thermodynamic and kinetic parameters for immersion freezing. The influence of the IN on the freezing process is either described using a contact-angle distribution among all IN (assuming that not all IN have the same influence on the freezing process) or by using a single contact angle for all IN and a fitted $\Delta g^#$ (assuming that the immersed IN influences the activation energy in a supercooled droplet). For both schemes the needed parameters were determined using IMCA/ZINC measurements for five types of mineral dust (microcline, ATD, kaolinite, montmorillonite, illite). Microcline is the most efficient IN and illite the least efficient.

The evolved IMCA CNT scheme for immersion freezing was implemented into ECHAM6-HAM2.

Testing immersion freezing schemes: Arctic case study

The framework of an Arctic measurement campaign with focus on mixed-phase clouds (M-PACE) was used as a testing platform for the parameterization schemes. The SCM setup of ECHAM6-HAM2 allows to constrain the meteorological conditions for the simulation and was therefore used for this case study to enable an easy comparison of different freezing schemes. The case study shows that the IMCA CNT scheme is sensitive to the time step of the model and very sensitive to the CNT parameters emerged from the fitting of laboratory data. Assuming the IN to be microcline (most efficient IN) instead of illite (least efficient IN) changes the model results significantly, due to the different freezing onset temperatures of the mineral dust types. The simulation results change less when using different parameterization schemes. However, the simulated amount of cloud ice by the CNT scheme differs from the empirical schemes based on laboratory experiments or field measurements. This difference is attributed to a stronger temperature dependence of the CNT scheme or its time dependence.
Outlook

There are several aspects which can be further elaborated to deepen the understanding of freezing parameterizations and their sensitivities in GCMs. This outlook focuses on three aspects: the further development of the IMCA CNT scheme for ECHAM6-HAM2 (mostly focusing on technical issues), further ideas for sensitivity tests for the scheme in the SCM setup and further analysis what could be done in the future.

1 Development of the IMCA CNT parameterization scheme in ECHAM6-HAM2

As described in chapters 5 and 6 some further development tasks listed below are suggested to improve the parameterization of immersion freezing:

- Coupling of the freezing scheme to the aerosol processing scheme.
  The aerosol processing scheme gives further information what happens with the aerosol particles inside the cloud. This would enable to estimate the number of activated aerosol particles explicitly and to deplete them explicitly with time. The number of IN is also known, which could be used to shift the contact angle distribution with time when a CNT-based approach with a contact angle distribution is used.

- Finding a suitable description of temperature which takes the small-scale processes, e.g. turbulence into account.
  This development may translate into improvements of the TKE-scheme.

- Testing the IMCA CNT scheme with different contact angle schemes.
  The IMCA CNT approach with a contact angle distribution or an \( \alpha(T) \) scheme still has to be tested in the SCM and can then be compared to the single \( \alpha \) IMCA CNT scheme and to the other parameterization schemes.

- Using a different type of contact angle distribution.
  It could be interesting to test if another distribution, e.g. the Gumbel distribution works better in terms of reproducing experimental freezing curves than the log-normal distribution for the contact angle distribution [analog to Sear (2013) and Savre and Ekman (2015)]. The Gumbel distribution is a distribution used in extreme-value analysis in cases where the sample is of exponential type.

- Truncating the contact angle distribution.
  When using a CNT-based approach with a contact angle distribution the contact angle distribution should change realistically with time. This could be done by truncat-
ing the distribution with every time step by using the number of ice crystals formed heterogeneously in the time step. However, this is straightforward if no new aerosol particles (IN) enter the cloud parcel, because otherwise it is possible that these new aerosol particles introduce supplementary efficient contact angles. This is always the case when the Wegener-Bergeron-Findeisen process is active, because activation of aerosol particles/diffusional growth of cloud droplets and diffusional growth of ice crystals does not happen at the same time in the model. If new aerosol particles are introduced into the cloud parcel, activation/diffusional growth of cloud droplets would take place prohibiting the Wegener-Bergeron-Findeisen process. Therefore, truncating the contact angle distribution could be connected to this process. Note that the contact angle distribution is not stored over time, so that this method could only be used from one to the next time step. Storing the Contact angle distribution is computationally to costly. It would be interesting to compare the results from a truncated $\alpha$-pdf scheme with the results from an $\alpha(T)$ scheme, which indirectly does account for a change of contact angle distribution with time. However, it should be checked first if the aerosol population is replenished and over which time span.

Sensitivity tests for the scheme

The sensitivity tests left important questions open. The understanding of parameterization sensitivities could be improved by:

- Testing the resolution dependence of the freezing parameterization.
  Concerning the vertical resolution it would be interesting to redo the sensitivity tests in the SCM (and probably also in the global setup) with more setups for the number of vertical levels to check if using significant more levels, e.g. 95 changes the freezing behavior in mixed-phase clouds. This could help to reproduce the liquid water layer on top of the mixed-phase clouds as observed during the M-PACE campaign. As the SCM has no horizontal resolution the sensitivity test for the horizontal resolution dependence has to be done when the schemes are used in the global setup.

- Testing the time step dependence of the freezing parameterization.
  Using smaller model time steps could help decide if a sub-time stepping is needed for the freezing process and which sub-time step would be sufficient. It is also necessary to test the effect of having a fixed time step versus using the model time step for more case studies and on a global scale.

- Testing the sensitivity of the freezing parameterization on the activation schemes.
  The number of activated particles is an important input parameter for most freezing parameterizations. Using the Abdul-Razzak and Ghan (2000) scheme instead of the Lin and Leaitch (1997) scheme might enhance freezing in mixed-phase clouds, be-
cause more aerosol particles are activated depending on size and composition of the aerosol particles. The dependence on size and composition of aerosol particles (in the Abdul-Razzak and Ghan (2000) scheme) may lead to enhanced regional differences of the freezing process.

- Testing the impact of IN depletion when using the aerosol processing scheme (as discussed above).

Further analysis

The new schemes, i.e. the IMCA CNT scheme, the Niemand et al. (2012) scheme, the DeMott et al. (2010) scheme and the DeMott et al. (2015) scheme still need to be validated and thoroughly tested in the global setup. For verification of the parameterization schemes the model output can be compared to local measurements and to satellite data of global coverage. Ground-based measurements, which can be used, are in-situ or filter measurements of ice nucleation/IN, lidar- or cloud radar measurements. To verify local measurements the SCM setup of ECHAM6-HAM2 can be used. The M-PACE campaign was not perfectly suited because dust was not the major IN there and it needs a lower freezing onset temperature than that prevalent during the campaign. An interesting test study could be a comparison with the Leipzig radar climatology. However, using point data to evaluate a GCM is always difficult, therefore the simulated IWP and LWP should also be evaluated against satellite data on a global scale.

After the validation of the IMCA CNT scheme it would be very interesting to do global sensitivity tests concerning the mineral dust type used as an IN and how using an efficient IN compares with a less efficient one in terms of the climate impact. Also a comparison of different freezing schemes and the impact on the climate on a regional and global scale could deliver some insight regarding the freezing schemes.

The results concerning the tests and comparison of the parameterization schemes shown in this thesis are only true for the case study presented and might not hold for other case studies or on the global scale. Therefore, some sensitivity tests should be re-evaluated using the global setup to be able to generalize the results.
### List of symbols and abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>J m(^{-2}) K(^{-1})</td>
<td>Fit parameter for (d\sigma_{\text{sw}}/dT)</td>
</tr>
<tr>
<td>(A_{\text{IN}})</td>
<td>m(^2)</td>
<td>Surface area of an IN</td>
</tr>
<tr>
<td>(A_{\text{tot.}})</td>
<td>m(^2)</td>
<td>Total surface area per unit volume of particles over all size bins</td>
</tr>
<tr>
<td>(A_{\text{tot.},j})</td>
<td>m(^2)</td>
<td>Total surface area per unit volume of particles in size bin (j)</td>
</tr>
<tr>
<td>(A_j)</td>
<td>m(^2)</td>
<td>Dust particle surface area in size bin (j)</td>
</tr>
<tr>
<td>(B)</td>
<td>J</td>
<td>Fit parameter for (\Delta g^#)</td>
</tr>
<tr>
<td>(c_p)</td>
<td>J kg(^{-1}) K(^{-1})</td>
<td>Specific heat of air</td>
</tr>
<tr>
<td>(C_{\text{prefac}})</td>
<td>m(^{-3}) s(^{-1})</td>
<td>Preexponential factor of the nucleation rate</td>
</tr>
<tr>
<td>(d)</td>
<td>m</td>
<td>Aerosol particle diameter</td>
</tr>
<tr>
<td>(D)</td>
<td>m(^2) s(^{-1})</td>
<td>Self diffusivity of water</td>
</tr>
<tr>
<td>(e_{\text{sw}}, e_{\text{si}})</td>
<td>Pa</td>
<td>Saturation vapor pressure over water and ice, respectively</td>
</tr>
<tr>
<td>(f)</td>
<td>-</td>
<td>Geometric term</td>
</tr>
<tr>
<td>(f, F)</td>
<td>J</td>
<td>(Specific) free energy</td>
</tr>
<tr>
<td>(g)</td>
<td>m s(^{-2})</td>
<td>Gravitational constant</td>
</tr>
<tr>
<td>(h)</td>
<td>J s</td>
<td>Planck constant</td>
</tr>
<tr>
<td>(J_{\text{hom}})</td>
<td>m(^{-3}) s(^{-1})</td>
<td>Homogeneous nucleation rate</td>
</tr>
<tr>
<td>(J_{\text{imm}})</td>
<td>m(^{-2}) s(^{-1})</td>
<td>Immersion freezing nucleation rate</td>
</tr>
<tr>
<td>(k_B)</td>
<td>J K(^{-1})</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>(K)</td>
<td>s(^{-1})</td>
<td>Rate of water molecules potentially transferring into an ice germ in the water volume</td>
</tr>
<tr>
<td>(L_{\text{in}}, L_v)</td>
<td>J kg(^{-1})</td>
<td>Latent heat of melting/vaporization</td>
</tr>
<tr>
<td>(n)</td>
<td>-</td>
<td>Number of molecules</td>
</tr>
<tr>
<td>(n_{\text{aer},0.5})</td>
<td>cm(^{-3})</td>
<td>Aerosol number concentration of particles with (d) larger than 0.5 (\mu)m</td>
</tr>
<tr>
<td>(n_{\text{IN}})</td>
<td>cm(^{-3})</td>
<td>IN number concentration</td>
</tr>
<tr>
<td>(n_{k, n_{k,\text{germ}}})</td>
<td>-</td>
<td>Number of water molecules in the ice embryo or germ</td>
</tr>
<tr>
<td>(n_s)</td>
<td>m(^{-2})</td>
<td>Number of water molecules in contact with the unit area of the ice germ</td>
</tr>
<tr>
<td>(n_s,\text{IN})</td>
<td>m(^{-2})</td>
<td>Surface density of active sites on an IN</td>
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<tr>
<td>(N_{\text{aer},\text{tot}})</td>
<td>-</td>
<td>Total number of aerosol particles larger than 35 nm</td>
</tr>
<tr>
<td>(N_A)</td>
<td>mol(^{-1})</td>
<td>Avogadro constant</td>
</tr>
<tr>
<td>(N_{\text{germ}})</td>
<td>-</td>
<td>Number of ice germs in the water droplet</td>
</tr>
<tr>
<td>(N_{\text{a,imm}})</td>
<td>-</td>
<td>Number of immersion freezing nuclei</td>
</tr>
<tr>
<td>(N_{\text{a,imm,dust}})</td>
<td>-</td>
<td>Number of dust immersion freezing nuclei</td>
</tr>
<tr>
<td>(N_{\text{a,imm,BC}})</td>
<td>-</td>
<td>Number of BC immersion freezing nuclei</td>
</tr>
<tr>
<td>(N_i)</td>
<td>-</td>
<td>Ice crystal number concentration</td>
</tr>
<tr>
<td>(N_{i,j})</td>
<td>-</td>
<td>Number of ice active aerosol particles in size bin (j)</td>
</tr>
<tr>
<td>(N_l)</td>
<td>m(^{-3})</td>
<td>Volume number density of water molecule in liquid water</td>
</tr>
<tr>
<td>(N_{\text{tot.},j})</td>
<td>-</td>
<td>Total number of aerosol particles in the size bin (j)</td>
</tr>
<tr>
<td>(p)</td>
<td>hPa</td>
<td>Pressure</td>
</tr>
<tr>
<td>(p(\alpha))</td>
<td>-</td>
<td>Probability density of contact angle (\alpha)</td>
</tr>
<tr>
<td>Symbol</td>
<td>Unit</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
<td>-------------</td>
</tr>
<tr>
<td>q</td>
<td>kg kg$^{-1}$</td>
<td>Specific humidity</td>
</tr>
<tr>
<td>$q_l$</td>
<td>kg kg$^{-1}$</td>
<td>Cloud liquid water mass mixing ratio in the cloud</td>
</tr>
<tr>
<td>r</td>
<td>m</td>
<td>Aerosol particles radius</td>
</tr>
<tr>
<td>$r_{embryo}$, $r_{germ}$</td>
<td>m</td>
<td>Radius of the ice embryo/ice germ (=critical radius)</td>
</tr>
<tr>
<td>r$_{IN}$</td>
<td>m</td>
<td>Radius of the IN</td>
</tr>
<tr>
<td>R</td>
<td>J mol$^{-1}$ K$^{-1}$</td>
<td>Universal gas constant</td>
</tr>
<tr>
<td>s, S</td>
<td>J</td>
<td>(Specific) entropy</td>
</tr>
<tr>
<td>$S_m$</td>
<td>J</td>
<td>Melting entropy</td>
</tr>
<tr>
<td>$S_i$</td>
<td>-</td>
<td>Saturation ratio with respect to ice</td>
</tr>
<tr>
<td>t</td>
<td>s</td>
<td>Time</td>
</tr>
<tr>
<td>T</td>
<td>K</td>
<td>Temperature</td>
</tr>
<tr>
<td>$T_0$</td>
<td>K</td>
<td>Melting point of water (273.15 K)</td>
</tr>
<tr>
<td>$T_c$</td>
<td>°C</td>
<td>Temperature in °</td>
</tr>
<tr>
<td>U</td>
<td>J</td>
<td>Internal energy</td>
</tr>
<tr>
<td>$V_{H_2O}$</td>
<td>m$^3$</td>
<td>Volume of a water molecule</td>
</tr>
<tr>
<td>$V_{ice}$</td>
<td>m$^3$</td>
<td>Volume of a water molecule in the ice embryo</td>
</tr>
<tr>
<td>$V_{ice}$</td>
<td>m$^3$</td>
<td>Volume of one gram molecule of ice</td>
</tr>
<tr>
<td>w</td>
<td>m s$^{-1}$</td>
<td>Vertical velocity</td>
</tr>
<tr>
<td>z</td>
<td>m</td>
<td>Height</td>
</tr>
<tr>
<td>Z</td>
<td>-</td>
<td>Zeldovich factor</td>
</tr>
<tr>
<td>$\Delta g^#$</td>
<td>J</td>
<td>Activation energy barrier</td>
</tr>
<tr>
<td>$\Delta G_k$</td>
<td>J</td>
<td>Gibbs free energy barrier</td>
</tr>
<tr>
<td>$\Delta t$</td>
<td>s</td>
<td>Time step</td>
</tr>
<tr>
<td>$\eta$</td>
<td>m$^2$ s$^{-1}$</td>
<td>Viscosity of water</td>
</tr>
<tr>
<td>$\mu$</td>
<td>rad</td>
<td>Mean contact angle of the contact angle distribution</td>
</tr>
<tr>
<td>$\mu_w$, $\mu_i$</td>
<td>J</td>
<td>Chemical potential of water and ice, respectively</td>
</tr>
<tr>
<td>$\rho_{air}$</td>
<td>kg m$^{-3}$</td>
<td>Density of air</td>
</tr>
<tr>
<td>$\rho_i$</td>
<td>kg m$^{-3}$</td>
<td>Surface density of ice</td>
</tr>
<tr>
<td>$\rho_l$</td>
<td>kg m$^{-3}$</td>
<td>Density of the cloud droplet</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>-</td>
<td>Variance of the contact angle distribution</td>
</tr>
<tr>
<td>$\sigma_{lw}$, $\sigma_{la}$, $\sigma_{wa}$</td>
<td>J m$^{-2}$</td>
<td>Interfacial tension between ice/water, ice/air, water/air, solid/air, solid/water</td>
</tr>
<tr>
<td>$\sigma_{sa}$, $\sigma_{sw}$</td>
<td>-</td>
<td>Interfacial tension at the ice water interface at 273.15 K</td>
</tr>
<tr>
<td>$\tau$</td>
<td>s</td>
<td>Dielectric relaxation time of water</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>rad</td>
<td>Contact angle</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>s$^{-1}$</td>
<td>Diffusive molecule flux to the ice germ</td>
</tr>
<tr>
<td>$\pi$</td>
<td>-</td>
<td>Ratio of a circle’s circumference to its diameter</td>
</tr>
<tr>
<td>$\omega$, $\omega_{largetscale}$</td>
<td>Pa s$^{-1}$</td>
<td>Vertical pressure velocity, large-scale contribution</td>
</tr>
<tr>
<td>$\Omega_{sm}$</td>
<td>m$^2$</td>
<td>Surface area per atom at interface</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>ACIPM</td>
<td>Aerosol Cloud Precipitation Interaction Model</td>
<td></td>
</tr>
<tr>
<td>AIDA</td>
<td>Aerosol interactions and dynamics in the atmosphere</td>
<td></td>
</tr>
<tr>
<td>ARM</td>
<td>Atmospheric Radiation Measurement</td>
<td></td>
</tr>
<tr>
<td>ATD</td>
<td>Arizona test dust</td>
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<td>BC</td>
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<td>CCN</td>
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<tr>
<td>CDNC</td>
<td>Cloud droplet number concentration ([l^{-1}])</td>
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<td>CFDC</td>
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<td>CNT</td>
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<td>Levitated drops in electrodynamic balance</td>
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<td>IN</td>
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<td>INUIT</td>
<td>Ice Nuclei Research Unit</td>
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<td>IWP</td>
<td>Ice water path ([g \ m^{-2}])</td>
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