

**ICE PARTICLE FORMATION  
IN THE LABORATORY AND  
IN THE ATMOSPHERE**



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Let me begin by saying that it is truly a great honor for me to have been awarded the *Prix Latsis Universitaires 2003 de l'Ecole Polytechnique Fédérale de Zurich*. I am deeply grateful to the Latsis Foundation for their generosity and encouragement. Thank you also for the opportunity to present my work to you.

## **Introduction**

I am sure that most of you have seen beautiful photographs of the Earth taken from satellites showing blue oceans and green continents with mountain tops covered with white snow. Such pictures are truly beautiful and provoke in most of us a feeling of awe for our planet. However, from a scientific standpoint many of these pictures do not show the Earth as it actually appears from space : clouds have been artificially removed from them. While it is a matter of taste whether pictures with or without clouds are more beautiful, it is clear that clouds cannot be ignored when it comes to understanding the processes occurring in the Earth's atmosphere. This is particularly important, because about one third of the Earth is covered with clouds at any given time. Clouds affect the composition of the atmosphere through removal of soluble trace gases and chemical reactions occurring in cloud droplets. Clouds also influence the global energy budget of the Earth. Everybody knows that we do receive less sunshine on a cloudy day. The same is true on a global scale and, hence, a better knowledge of the formation processes of clouds are important for our understanding of the Earth's greenhouse effect and future climate.

## **Ice and Water**

My scientific work is mainly concerned with a one particular group of clouds : those that consist of ice particles. Examples for clouds containing ice particles are cirrus clouds in the upper troposphere (7-16 km) or polar stratospheric clouds in the lower stratosphere (15-25 km). Persistent contrails induced by high flying aircrafts also consist of such ice particles. To understand under which conditions ice particles can form and exist in the atmosphere we have to look more closely into the properties of water and ice. Water occurs in the atmosphere in all three physical states : gaseous water vapor, liquid water, and crystalline ice. Which

of these three phases is the thermodynamically preferred state can be determined with the help of a so-called phase diagram. Such a phase diagram is something like a « map of waterworld », with each of the three countries gasland, liquidland, and solidland representing one of the three possible phases of water. We know from daily experience that temperature determines which is the preferred stable state of water at atmospheric pressure: below  $0^{\circ}\text{C}$ , ice is the preferred state of water molecules, between 0 and  $100^{\circ}\text{C}$  it is liquid water, and above  $100^{\circ}\text{C}$  it is water vapor. In our map of waterworld, these temperatures determine the location of the borders between the different countries, e.g., the solidland/liquidland border is located at  $0^{\circ}\text{C}$  and the liquidland/gasland border is located at  $100^{\circ}\text{C}$ . Water molecules can travel between different countries, thereby changing their physical state in what is called a phase transition. Liquid water molecules cooled below  $0^{\circ}\text{C}$  are supposed to freeze into an ice crystal at the border, and the water molecules in an ice crystal are supposed to melt into liquid water when heated to temperatures above  $0^{\circ}\text{C}$ . Hence, in theory the border temperatures determine whether or not water molecules are supposed to melt or freeze. In reality, however, not all water molecules obey these thermodynamic rules. While water molecules in ice crystals do indeed melt at  $0^{\circ}\text{C}$ , liquid water molecules can be cooled to temperatures much below  $0^{\circ}\text{C}$ . This ability of liquid water to supercool has been known for quite some time. The earliest observations of supercooled water have been reported in a publication by Fahrenheit in 1724. In experiments that Fahrenheit performed on March 2-4, 1721 he was able to supercool water to about  $-9.4^{\circ}\text{C}$ . Today, with more elaborate experiments, we can supercool water to about  $-38^{\circ}\text{C}$  before ice freezing occurs. From a number of experimental studies we have learned over the past decades that the temperature at which freezing occurs in real water samples is determined by kinetics and involves a nucleation process. Typically, the nucleation of the ice is initiated at the surface of a solid nucleus present in the liquid water. On the other hand, a water samples devoid of any such nuclei can also nucleate spontaneously by forming a stable ice germ through internal fluctuations. The latter process is called homogeneous ice nucleation and is the process responsible for the freezing of water samples at about  $-38^{\circ}\text{C}$ . Such large supercoolings are only possible in very clean water samples a few micrometers in size (a few thousands of a millimeter!).

## **Aerosols and Atmospheric Ice Formation**

Interestingly, field measurements with aircrafts or balloons have shown that atmospheric water droplets in clouds do indeed sometimes freeze to ice at temperatures of about  $-38^{\circ}\text{C}$  implying that homogeneous ice nucleation is the dominant freezing process in such cases. However, most of the time, ice particle formation in the atmosphere does not occur in water droplets but rather occurs in aerosol particles. Atmospheric aerosol particles are solid or liquid particles suspended in air. Their size varies considerably, but typically they are smaller than one micrometer in size. All clouds in the atmosphere form on such aerosol particles and, therefore, the conditions at which clouds form are strongly dependent on the properties of the preexisting aerosol particles. Aerosols can consist of a huge variety of substances. In the upper troposphere and lower stratosphere ( $\sim 7\text{--}25\text{ km}$ ) liquid aerosol particles contain dissolved substances such as ammonia, sulfates, nitrates, or organics. Hence, in order to understand the formation of ice particles at such altitudes, we need to understand the effect that dissolved solutes have on the homogeneous ice nucleation temperature of water.

### **Laboratory Experiments**

This was the motivation for us to develop a new technique suitable of studying ice nucleation in small micrometersized droplets containing various solutes of atmospheric importance. The new technique works in the following way : a stream of high pressure gas is passed over a tiny syringe capillary containing an aqueous solution, resulting in a fine spray of numerous very small aerosol droplets. Some of these droplets are then deposited on a glass slide. In order to avoid any contamination with room air the droplets are protected in a small cell about one millimeter in diameter. This cell is positioned under an optical microscope, where the individual droplets can be observed visually. The microscope is equipped with a cooling device so that the droplets can be cooled until freezing is observed, i.e., small ice crystals form in the liquid droplets. In principle, this technique allows us to determine the homogeneous ice nucleation temperature for each particular class of droplets. But how can we be sure, that the observed freezing temperature in such an experiment is indeed the homogeneous ice nucleation

temperature ? First, the glass slide in contact with the droplets is specially treated with an organosilane in order to minimize any interaction between the glass surface and the supercooled aqueous droplets. Secondly, we have performed many experimental tests with our apparatus and found that freezing in pure water droplets does occur at  $-38^{\circ}\text{C}$ , i.e., at the homogeneous ice nucleation temperature for water. After these successful test measurements, we have performed such type of microscope experiments for droplets containing many different solutes at various solute concentrations. We found that the homogeneous ice nucleation temperature is shifted to lower temperatures by the addition of solutes : the higher the solute concentration, the lower is the homogeneous ice nucleation temperature of the droplets. For example, droplets containing about one part of sulfuric acid in three parts of water freeze at the extremely low temperature of  $-100^{\circ}\text{C}$ , which is about the lowest temperature that occurs in the lower 50 km of our atmosphere. In addition to these microscope experiments, we have used another technique, in which small droplets are produced in the form of a waterin oil emulsion. Such emulsions consist of small aqueous droplets contained in an inert oil matrix. (The most familiar type of emulsion in our daily life is probably a mayonnaise, which is an oil-in-water emulsion, i.e., small oil droplets surrounded by a water matrix.) Our waterin oil emulsions contain water droplets that are only a few micrometers in size, and, hence, can also be used to determine the homogeneous ice nucleation temperature of water and aqueous solutions. To our reassurance, the results obtained from the microscope technique agree very well with those from the emulsion experiments. When we evaluated the data of our experiments with various solutions together with additional data from the literature we observed something very interesting. None of the aqueous solutions obey the law that ice freezing should occur at the border between liquidland and solidland. Instead, there seems to be another kind of law that determines how far aqueous solutions can be supercooled before homogeneous ice nucleation occurs. We found that all of the solutions that we looked at obey this new « homogeneous ice nucleation law » : solutions of acids and salts, solutions of dissociating or nondissociating organics, and polymers. We used these data, together with data of pure water and aqueous solutions under mechanical pressure, to develop a new ther-

thermodynamic wateractivitybased ice nucleation theory. In this theory, homogeneous ice nucleation in aqueous solutions is dependent on temperature and the water activity of the solution, but is independent of the nature of the dissolved solutes.

### **Atmospheric Ice Nucleation**

One of the major advantages of our new theory is, that it can be used to predict the conditions for ice nucleation in liquid atmospheric aerosol droplets without prior knowledge of the composition of the aerosols. We have compared the predictions of our theory with field measurements of ice clouds in the atmosphere. These include cirrus ice clouds at altitudes of 8 and 12 km, as well as polar stratospheric clouds at an altitude of about 22 km. To our surprise these measurements do agree very well with the predictions by our theory (that is based on our laboratory experiments). We can conclude from this agreement that, first, our theory is indeed applicable to the atmospheric situation, and, secondly, that atmospheric ice clouds in the upper troposphere and lower stratosphere do indeed quite often form via a homogeneous ice nucleation process.

### **Summary and Conclusions**

In summary, we have performed laboratory experiments on ice nucleation in micrometersized water and aqueous solution droplets. The results of these experiments have been used to develop a thermodynamic theory for homogeneous ice nucleation in water and aqueous solution droplets. We have employed this theory to predict the formation of atmospheric ice clouds. The good agreement between predictions and cloud observations shows that our theory is applicable to atmospheric ice cloud formation processes that occur on the km scale. Basically what we have done is to produce little ice clouds in the laboratory, i.e., we have simulated the atmospheric ice nucleation process in laboratory experiments. Once we understood the fundamental underlying mechanisms and the conditions at which ice nucleation commences, we have used this knowledge to predict the conditions at which ice nucleation is expected to occur in the actual atmosphere. In the meantime, our theory has been employed by other groups in larger

scale atmospheric models. These models employ our theory to predict ice cloud formation on a global scale in order to better understand such important atmospheric problems as the chemistry occurring in the ozone hole or to simulate the present and future climate of the Earth. This application is also what does fascinate me the most about this work : that small scale processes such as ice nucleation in a micrometersized droplet can be used to gain a better understanding of important atmospheric problems of global proportions.

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