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Abstract

Microphysics of Atmospheric Aerosols: Phase Transitions and Cloud Formation Mechanisms

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ABSTRACT

Clouds play an extremely important role in our atmosphere, from controlling the local weather, air pollution and chemical balance in the atmosphere to affecting long-term climatic changes at local, regional and global scales. The mechanisms through which tropospheric clouds form are still not fully understood, leading to gross uncertainties in understanding the effect of atmospheric aerosols on the environment. Using laboratory measurements, microphysical properties of typical micro-meter size atmospheric aerosols are investigated in this study.

Upper tropospheric ice clouds (cirrus) form when ice is nucleated either homogeneously or heterogeneously in aqueous aerosols. We have investigated the homogeneous and heterogeneous ice nucleation in aqueous particles.

Our results for homogeneous nucleation in aqueous ammonium nitrate particles show that the current thermodynamic models do not correctly predict water activities in these particles under super-saturated conditions. High super-saturations are required for ice to nucleate homogeneously in aqueous ammonium nitrate particles.

We have also investigated the role of crystallized salt cores, such as solid ammonium sulfate and leteovite, in the heterogeneous nucleation of ice in saturated aqueous ammonium sulfate particles. Our results show that the surface morphology and defects on microcrystals could result in the creation of active sites, leaving the crystallized salt cores as potent ice nuclei under certain conditions. We have also investigated the role of mineral dust and soot, major components of insoluble particulates in the atmosphere, as ice-nuclei. We have found mineral dust to be an effective ice nuclei but both fresh and aged soot do not promote ice nucleation in aqueous particles.

Soot is the most ubiquitous aerosol in the atmosphere. The lifetime and microphysics of nano-porous soot has a large impact on earth’s radiative budget, heterogeneous chemistry, urban and regional air pollution and human health. We have investigated the hydrophilic properties of both fresh and aged soot as a function of relative humidity. Our results show that fresh hydrophobic soot oxidized (aged) by OH/O3/UV in the presence of water vapor or by exposure to concentrated HNO3 becomes hydrophilic and exhibits a greater affinity for water. Due to this increased hydrophilicity, aged soot can be easily entrained inside existing liquid cloud droplets, and even activate as cloud condensation nuclei at high super-saturations, thus influencing its heterogeneous chemistry, radiative properties and atmospheric lifetime.
# TABLE OF CONTENTS

Abstract ........................................................................................................................................... 3

Table of Contents ............................................................................................................................. 4

Acknowledgements .......................................................................................................................... 7

CHAPTER 1 ..................................................................................................................................... 9

Introduction ..................................................................................................................................... 9
1.1 Tropospheric aerosols .............................................................................................................. 9

CHAPTER 2 .................................................................................................................................... 14

Background ..................................................................................................................................... 14
2.1 Types of clouds in the troposphere .......................................................................................... 14
2.2 Liquid clouds ............................................................................................................................. 16
   2.2.1 Importance of liquid clouds ............................................................................................. 16
2.3 CCN activation .......................................................................................................................... 17
2.4 Cirrus clouds ............................................................................................................................. 24
   2.4.1 Importance of cirrus clouds ............................................................................................. 24
   2.4.2 Liquid-to-solid phase transitions: ................................................................................... 25
   2.4.2.1 Homogeneous Nucleation ......................................................................................... 26
   2.4.2.2 Heterogeneous Nucleation ....................................................................................... 29

CHAPTER 3 .................................................................................................................................... 33

Homogeneous nucleation of ice in NH₄NO₃/H₂O particles ............................................................. 33
3.1 Background .............................................................................................................................. 33
3.2 Experimental ........................................................................................................................... 35
   3.2.1 Optical Microscope ....................................................................................................... 36
   3.2.2 Differential Scanning Calorimetry ................................................................................ 41
3.3 Results ...................................................................................................................................... 42
3.4 Discussion ............................................................................................................................... 43

CHAPTER 4 .................................................................................................................................... 50

Heterogeneous nucleation by crystallized salt cores ...................................................................... 50
4.1 Experimental ................................................................. 51
   4.1.1 Ammonium Sulfate Experiments ............................... 51
   4.1.2 Ammonium Bisulfate Experiments .............................. 53
4.2 Results and Discussion ............................................... 55
   4.2.1 Ammonium Sulfate ............................................... 55
   4.2.2 Ammonium Bisulfate ............................................ 66

CHAPTER 5 ............................................................................ 70
Heterogeneous nucleation of ice by mineral dust ..................... 70
5.1 Experimental ............................................................... 72
5.2 Results ........................................................................ 74
5.3 Discussion ................................................................. 75

CHAPTER 6 ............................................................................ 87
Heterogeneous nucleation of ice by soot ................................. 87
6.1 Background .................................................................. 87
6.2 Experimental ............................................................... 90
   6.2.1 Optical Microscopy .................................................. 90
   6.2.2 Scanning Electron Microscopy and Energy Dispersed X-ray
        Spectroscopy ............................................................. 91
   6.2.3 Soot-generation ...................................................... 92
   6.2.4 Oxidation ............................................................. 97
      6.2.4.1 OH/O_3/UV Exposure in the Presence of H_2O ...... 99
      6.2.4.2 Exposure to HNO_3 ......................................... 102
6.3 Results and discussion .................................................. 104

CHAPTER 7 ............................................................................ 108
Changes in hydrophilic properties of soot ............................... 108
7.1 Introduction ................................................................. 108
7.2 Experimental ............................................................... 112
   7.2.1 Soot preparation .................................................... 112
   7.2.2 Oxidation ............................................................ 112
   7.2.3 Quartz Crystal Microbalance .................................... 113
   7.2.4 Light Reflectometry ................................................. 114
   7.2.5 Environmental Scanning Electron Microscopy ............. 117
7.3 Results and Discussion .................................................. 118
   7.3.1 Water uptake on soot surfaces at RH < 100% ................. 118
   7.3.2 Water uptake on soot surfaces at RH ≥ 100% .............. 122
7.4 Conclusion ................................................................. 129

CHAPTER 8 ............................................................................ 130
Final Remarks .................................................................... 130
8.1 Conclusions ............................................................... 130
8.2 Ideas for future research ......................................................... 132

References .................................................................................. 134
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Chapter 1

INTRODUCTION

1.1 Tropospheric aerosols

Aerosol is the term used to define suspensions of solid or liquid particles in a gas. In atmospheric sciences, the terms particle and aerosol is often used to indicate condensed phase material in the atmosphere. Particles that are ejected directly into the atmosphere are called primary aerosols, whereas particles that form in-situ via chemical reactions are called secondary aerosols. Aerosol particles vary greatly in size, source, chemical composition, amount and distribution in space and time, and how long they survive in the atmosphere. The role of aerosols in atmospheric physical and chemical processes is determined by their number concentration, mass, size, chemical composition, and aerodynamic and optical properties [Finlayson-Pitts and Pitts Jr., 2000].
Aerosols play a major role in atmospheric chemistry by engaging in heterogeneous multi-phase reactions [Finlayson-Pitts and Pitts Jr., 2000; Seinfeld and Pandis, 1998] and providing the central link between gas-phase chemistry and cloud cover. Figure 1-1 illustrates some of the complex interactions in atmospheric chemistry that involve aerosols. Aerosols exert a dramatic effect on Earth’s radiation budget and albedo, precipitation and desertification, cloud formation and lifetime, and human health. During the last millennium, a shift of ~1% has been observed in the energy balance between absorption of incoming solar radiation and emission of thermal radiation from the Earth’s system. This effect, also known as climate change, is most impacted by anthropogenic greenhouse gases and atmospheric aerosols. Whereas greenhouse gases mainly warm the Earth’s surface by trapping outgoing thermal radiation, aerosols mainly reflect and absorb solar radiation, as well as affect cloud properties [Kaufman et al., 2002]. Climate models that try to simulate the changes in Earth’s temperatures, have shown uncertainties ranging from -0.4 Wm⁻² to -1.5 Wm⁻² in forcing by sulfate aerosols associated with changes in drop size distributions of atmospheric aerosols [Chuang et al., 1997]. Changes in droplet concentrations due to carbonaceous aerosols from biomass burning and fossil fuel/industry have lead to estimates of forcing that range from -1.2 to -1.6 Wm⁻² depending on the magnitude of natural organics assumed in the

![Figure 1-1: Interaction between gas-phase chemistry, tropospheric aerosols and tropospheric clouds](image-url)
calculation[Penner et al., 1998]. Changes in the magnitude of natural sources of dust and sea salt could further change this estimate by a factor of 2 which can double if the total life-time and extent of clouds is affected[Tegen et al., 1996]. Thus, the total indirect forcing by anthropogenic aerosols may range from about –0.3 to –3.0 Wm\(^{-2}\). Given that the total radiative forcing by major greenhouse gases is estimated at \(~2.57\) Wm\(^{-2}\)[Finlayson-Pitts and Pitts Jr., 2000; IPCC, 1996], the potential impact of aerosols could be huge.

Aerosols in the atmosphere can be composed of a wide variety of materials depending on the location where they are found[Finlayson-Pitts and Pitts Jr., 2000; Seinfeld and Pandis, 1998]:

**Water only:** clusters, cloud particles, and rain droplets.

**Marine:** saline water from the oceans and tidal action, and biogenic compounds from algal bloom and decay. Composition includes metal halides, sulfates and organic compounds.

**Natural:** desert sands, rock weathering, soil erosion, volcanoes and biogenic emissions. Composition includes alumino-silicates, ores, clays, organic matter, viruses, bacteria and soot.

**Anthropogenic:** chemical emissions, fossil fuel combustion and heavy industry. Composition includes soot, fuels and heavy metals.

Aerosols are found ubiquitously in the atmosphere and typical concentrations can be as high as \(10^8\) cm\(^{-3}\). Typical particle diameters range from 0.001 \(\mu\)m to 100 \(\mu\)m, even though particles larger than 10 \(\mu\)m are generally active as cloud particles. The U.S. Environmental Protection Agency has classified particles according to their diameters: PM\(_{10}\) for particles with diameters < 10 \(\mu\)m, and PM\(_{2.5}\) for diameters < 2.5 \(\mu\)m. Particles with diameters > 2.5 \(\mu\)m are known as coarse particles which those with diameters < 2.5 \(\mu\)m are called fine particles. Approximately 30 % of the particulate mass in non-urban (rural, remote and marine) areas and 50 % of urban aerosols are fine particles[Finlayson-Pitts and Pitts Jr., 2000].
Figure 1-2 illustrates some of the processes that lead to the creation and removal of atmospheric aerosols. In order to balance the rate at which aerosols are emitted into the air, there are natural ways in which they are removed from the atmosphere. These processes include wet deposition (rainout, washout, sweepout, occult deposition) and dry deposition (gravitational settling, turbulent settling). In the case of dry deposition, the aerosol’s fall speed becomes larger than the gravitational pull and the aerosol settles out of the atmosphere. During wet deposition, the aerosol gets transformed (or embedded) into a cloud particle, which is then removed from the atmosphere in the form of rain, snow, hail, etc. Wet deposition of aerosols may occur in several steps, each of which represents phase transformations that the aerosol mass undergoes, for example: deliquescence, efflorescence, CCN activation, evaporation and freezing. The objectives of this thesis are to study the hydrophilicity and freezing of aerosols in the troposphere. Specifically, the ability of processed (aged) carbonaceous soot particles to activate as CCN under atmospheric conditions, entrapment of aged soot in existing liquid cloud particles, and the homogeneous/heterogeneous nucleation of ice in inorganic aqueous
particles will be investigated. To do so, several experimental methods have been employed, including optical microscopy, differential scanning calorimetry, environmental scanning electron microscopy and light reflectometry. The experimental systems allow for studies to be conducted under controlled laboratory conditions that can be extrapolated to atmospheric conditions of temperature and relative humidity.
Chapter 2

BACKGROUND

2.1 Types of clouds in the troposphere

Clouds play an extremely important role in our atmosphere, from controlling the local weather, air pollution and chemical balance in the atmosphere to affecting long-term climatic changes at local, regional and global scales. Clouds have been of interest to humans for a very long time – from the ancients who encountered fog in valleys and mountains to the early development of meteorology that date back almost 2500 years. It is considered that as far back as circa 500 B.C., Anaxagoras of Clazomenae [Ball, 2001] had already deduced that clouds were made of both water and ice particles. For a cloud to form, it is necessary that a large volume of air be cooled below its dew point. In the atmosphere, this cooling occurs by adiabatic expansion of ascending air, by radiative cooling, or by the mixing of air masses with different temperatures and humidities. Continued cooling leads to condensation and precipitation, and if temperatures drop below freezing point, ice formation may occur in aqueous particles. The formation mechanisms of clouds have been studied for a long time but they are far from being understood completely, especially the transformation of atmospheric aerosols into cloud droplets and the formation of ice clouds by freezing of cloud droplets.
Clouds are classified according to their phase (liquid or solid), morphology and altitude at which they occur. In 1802, Jean-Baptiste Lamarck (1744-1829) [Ball, 2001] published the first scientific cloud classification system based on morphology. In 1803, Luke Howard published a cloud classification system using Latin names which is still in use, and it was not until 1887 that Hildebrandsson and Abercrombie firmly established height as an important classification parameter for clouds [Ball, 2001]. By international agreement, the World Meteorological Organization (WMO) now has the responsibility and authority to classify clouds. Some of the more prevalent tropospheric cloud types include:

**Low level clouds**

* Nimbostratus: Nimbostratus clouds are typically dark gray in color and associated with light to moderate precipitation. They are comprised of water droplets since their bases lie below 2 km. When temperatures are cold enough, nimbostratus may contain ice particles and snow.

**Mid level clouds**

* Altocumulus: Altocumulus typically forms from the gradual lifting of air and have the appearance of puffy masses or parallel bands. They form 3-4 km above the ground and typically one portion of the cloud is darker than the rest, which makes them distinguishable from the higher cirrocumulus.

* Stratocumulus: Stratocumulus clouds are generally low, lumpy clouds. They range in color from dark gray to light gray and can appear in rows, patches, or as rounded masses with breaks of clear sky in between. Rain or snow rarely falls from these clouds and they are larger than altocumulus in appearance.

**High Level clouds**

* Cirrostratus: Cirrostratus clouds are often thousands of feet thick and cover the entire sky. They are, however, relatively transparent and the sun or moon may be seen through them.
**Cirrus:** Cirrus Clouds form around 8-15 km above the Earth’s surface. They are primarily composed of ice crystals due to the cold temperatures at this height and are typically white in color with wispy features.

### 2.2 Liquid clouds

#### 2.2.1 Importance of liquid clouds

Earth’s radiative balance is maintained by the energy that reaches Earth in the form of solar radiation and the thermal energy that radiates back into the atmosphere from the Earth. Aerosols in the atmosphere affect the Earth’s radiative balance in *direct* and *indirect* ways ([IPCC, 1996](#)). Whereas greenhouse gases present in the atmosphere reduce the emission of thermal radiation to space, and hence contribute to the warming of the Earth, aerosols mainly reflect and absorb solar radiation (direct aerosol effect) and modify the properties of clouds (indirect aerosol effect) ([IPCC, 1996](#)).

The physical and chemical properties of clouds have a strong impact on the Earth’s weather and climate. The indirect effect of the aerosols in the atmosphere is largely related to the ability of some, but not all, aerosol particles in the atmosphere to act as cloud condensation nuclei (CCN). Aerosol particles are called cloud particles (found either in liquid or frozen state) once they have grown to a certain size via condensation of water vapor on the particles ([Pruppacher and Klett, 1997](#)). Modifications to the properties and characteristics of clouds in the atmosphere have both cooling and warming effects on the atmosphere and Earth’s surface. Low-lying, thick clouds primarily reflect solar radiation and cool the surface of the Earth by reducing the amount of solar radiation reaching the surface. High, thin and wispy clouds primarily transmit incoming solar radiation but trap some of the outgoing infrared radiation emitted by the Earth and radiate it back downward, thereby warming the surface of the Earth ([Finlayson-Pitts and Pitts Jr., 2000; Pruppacher and Klett, 1997; Seinfeld and Pandis, 1998](#)). Cloud particles containing dust, black carbon, graphite and soot are dark and strongly absorb incoming light ([Finlayson-Pitts and Pitts Jr., 2000](#)). The effects of this type of clouds are two-fold, both warming the atmosphere and cooling the surface.
Whether a given cloud system leads to the cooling or warming of the surface is dependant on several factors, including the cloud altitude, cloud number density, size, and composition. In addition, since the presence of large number of aerosols in polluted regions results in sharing of the condensed water during cloud formation, precipitation patterns and cloud lifetimes are also modified. Changes in precipitation patterns and cloud lifetimes may be responsible for increased floods, desertification, drought and disease at local and regional levels. The radiative effects of clouds are poorly characterized with an uncertainty 5 to 10 times larger than the uncertainty in predicted warming by greenhouses gases. The effects on precipitation patterns or human health are even less well-understood[Kaufman et al., 2002].

2.3 CCN activation

Cloud particles form via condensation of water vapor into liquid drops. Classical Nucleation Theory (CNT) attempts to describe the condensation process as a phenomenological reaction rate at which the first step in the phase transition takes place. The classical nucleation theory is explained in detail by reviews in Seinfeld and Pandis[Seinfeld and Pandis, 1998] and Pruppacher and Klett[Pruppacher and Klett, 1997].

The first step in the gas to liquid phase transition is the formation of small molecular clusters upon which other molecules can condense. These molecular clusters are formed as result of fluctuations in the ensemble and remain in equilibrium with the gaseous vapor. When the size of the molecular clusters exceeds a critical value, they grow spontaneously and the formation of critical size cluster is called nucleation. In a one component gaseous system (e.g. water), if the total number of molecules in the gas phase are $N_T$ and $i$ molecules constitute the liquid cluster, the number of gaseous molecules remaining is given by $n_g = N_T - i$. Then if $\mu_{gas}$ and $\mu_{liq}$ are the Gibbs free energies of a molecule in the gaseous and liquid phases respectively,

\begin{equation}
\Delta G = n_g \mu_{gas} + i \mu_{liq} + 4 \pi r_i^2 \sigma_{g-l} - N_T \mu_{gas}
\end{equation}
where $4\pi r_i^2 \sigma$ is the free energy associated with an interface with radius of curvature $r_i$ and surface tension $\sigma$. This equation, used because we are considering a gas-liquid phase transition, can be re-written as

**Equation 2-2**

$$\Delta G = i(\mu_{liq} - \mu_{gas}) + 4\pi r_i^2 \sigma$$

Note that the number of molecules in the liquid cluster, $i$, and the drop radius $r_i$ are related by

**Equation 2-3**

$$i = \frac{4\pi r_i^3}{3\nu_{liq}}$$

where $\nu_{liq}$ is the volume occupied by a molecule in the liquid phase. Thus, combining the above two equations we get

**Equation 2-4**

$$\Delta G = \frac{4\pi r_i^3}{3\nu_{liq}} (\mu_{liq} - \mu_{gas}) + 4\pi r_i^2 \sigma$$

In order to calculate the difference in the molecular Gibbs free energies, we use the Gibbs-Duhem equation at constant temperature and acknowledging that $dn_i=0$:

**Equation 2-5**

$$dG = -SdT + Vdp + \sum_{i=1}^{k} \mu_i dn_i$$

which tells us that $dG=(\nu_{liq}-\nu_{gas})dp$. Since $\nu_{gas}>>\nu_{liq}$ when a small nuclei forms, we can assume $\nu_{liq}-\nu_{gas}=-\nu_{gas}$, giving $dG=-\nu_{gas}dp$. Assuming the vapor phase to be ideal, we get $\nu_{gas}=kT/p$. Integrating, we find:
Figure 2-1: $\Delta G$ versus radius of particle

Equation 2-6

$$\mu_{\text{liq}} - \mu_{\text{gas}} = -kT \int_{r_i}^{r_s} \frac{p_s dp}{\gamma_s}$$

where $p_A^o$ is the vapor pressure of pure A over a flat surface, and $p_A$ is the actual equilibrium partial pressure over the liquid. Hence we find that

Equation 2-7

$$\mu_{\text{liq}} - \mu_{\text{gas}} = -kT \ln \frac{P_A}{P_A^o}$$

where the ratio $P_A/P_A^o$ is the saturation ratio $S$.

Combining the above equations, the following expression for Gibbs free energy change is found for the formation of a critical cluster:

Equation 2-8

$$\Delta G_i = -\frac{4\pi r_i^3}{3\Omega_{\text{liq}}^i} kT \ln S + 4\pi r_i^2 \sigma_{\text{liq}}$$

The first term in the equation corresponds to the transfer of molecules from the gaseous to the liquid phase, and the second one to the formation of an interface.
Figure 2-1 shows the Gibbs free energy of formation of a liquid cluster as a function of its radius. The surface free energy term in equation above is always positive because creating a surface requires work. When $S < 1$, the two energy terms are positive and $\Delta G_i$ increases continually; i.e. the cluster is unstable and the liquid will evaporate. On the other hand when $S > 1$, the first term in above equation is negative; therefore $\Delta G_i$ has a maximum with respect to $r_i$.

Setting $\frac{d\Delta G_i}{dr_i} = 0$ gives us

\[ 8\pi \sigma_{iw} r - \frac{4\pi kT \ln S}{\nu_{liq}} r^2 = 0 \]

\textbf{Equation 2-9}

The cluster with the maximum $\Delta G_i$ is called a critical cluster and its properties are as follows:

\[ r^* = \frac{2\sigma_{iw} \nu_{liq}}{kT \ln S} \]

\textbf{Equation 2-10}

Equation 2-10 is also called the \textit{Kelvin} equation.

\[ i^* = \frac{32}{3} \pi \nu_{liq}^2 \left( \frac{\sigma_{iw}}{kT \ln S} \right)^1 \]

\textbf{Equation 2-11}

\[ \Delta G^* = \frac{16}{3} \pi \sigma_{iw}^3 \left( \frac{\nu_{liq}}{kT \ln S} \right)^2 \]

\textbf{Equation 2-12}

where $r^*$ is the critical radius of the cluster, $i^*$ is the number of molecules in the critical cluster and $\Delta G^*$ is the free energy of formation of the critical cluster. The \textit{Kelvin} equation can also be written as
Equation 2-13

\[ \frac{p_A}{p_A^*} = \exp \left( \frac{2 \sigma_{lg} V_{lg}}{kT r} \right) \]

The Kelvin equation states that the vapor pressure over a droplet depends exponentially on the inverse of the droplet radius. Therefore, as the radius of a drop decreases, the vapor pressure over the droplet increases as compared to that over bulk flat liquid. This equation is also true for water droplet that contains an insoluble sphere inside.

As mentioned above, nucleation is the first step in the condensation process. However, the size of the initial cluster formed from the gas phase into liquid is very small, and according to the Kelvin equation, the vapor pressure over the cluster would be so large that it would evaporate immediately except at extremely high super saturations which are unrealistic for the atmosphere. As a result, clouds only form in the presence of pre-existing particles (aerosols) upon which water could initially condense. These particles, which provide stability to the condensed water clusters are called cloud condensation nuclei, CCN. Upon reaching a critical relative humidity (super-saturation), the CCN particles activate, i.e. continue to take water indefinitely and become cloud particles.

The ability of an aerosol to act as a CCN depends on a few basic physical-chemical principles. These are the Kelvin effect (increased vapor pressure over a droplet), as described above, and the lowering of vapor pressure of a solvent by a non-volatile solute (Raoult's law).

Raoult's law states that the vapor pressure of a solution component \( w \) (for water), whose pure vapor pressure is \( p_w^* \) is proportional to its mole fraction in solution, \( x_w \), i.e.

Equation 2-14

\[ p_w = \gamma_w x_w p_w^* \]

where \( \gamma_w \) is the water activity coefficient and \( x_w \) is the mole fraction of water in the solution. Substituting the above expression into the Kelvin equation gives us
Equation 2-15

\[ \frac{p_w}{p_w^o x_w} = \exp \left( \frac{2 \sigma \nu_{ij}}{kTr} \right) \]

If \( n_w \) and \( n_s \) are the moles of water and moles of solute respectively, and \( \nu_w \) and \( \nu_s \), the partial molar volumes of the two components in the solution, the droplet volume satisfies the equation

Equation 2-16

\[ \frac{4}{3} \pi r^3 = n_w \nu_w + n_s \nu_s \]

Since \( x_w = \frac{n_w}{n_w + n_s} \), we get

Equation 2-17

\[ \frac{1}{x_w} = 1 + \frac{n_s}{n_w} = 1 + \frac{n_s \nu_w}{4/3 \pi r^3 - n_s \nu_s} \]

The Kelvin equation, hence becomes,

Equation 2-18

\[ \ln \frac{p_w}{p_w^o} = \frac{2 \sigma \nu_{ij}}{kTr} + \ln \gamma_w - \ln \left( 1 + \frac{n_s \nu_w}{4/3 \pi r^3 - n_s \nu_s} \right) \]

If the solution is dilute, the volume occupied by the solute can be neglected, relative to the droplet volume and the above equation can be simplified to

Equation 2-19

\[ \ln \frac{p_w}{p_w^o} = \frac{2 \sigma \nu_{ij}}{kTr} + \ln \gamma_w - \ln \left( 1 + \frac{3n_s \nu_w}{4 \pi r^3} \right) \]

For dilute solutions, one can also assume that \( \gamma_w \to 1 \) and \( \ln(1+x) \approx x \) as \( x \to 0 \).

Hence, we get
Equation 2-20

\[ \ln \frac{p_w}{p_w^0} = \frac{2\sigma_{lw} V_{lw}}{kTr} - \frac{3n_w V_w}{4\pi r^3} \]

with \( A = \frac{2\sigma_{lw} V_{lw}}{kT} \) and \( B = \frac{3n_w V_w}{4\pi} \). It is customary to write Equation 2-20 as

Equation 2-21

\[ \ln \frac{p_w}{p_w^0} = \frac{A}{r} - \frac{B}{r^3} \]

![Graph showing Kohler's curves for typical inorganic salts](image)

Figure 2-2: Kohler's curves for typical inorganic salts [Seinfeld, 1998].

which can also be expressed as saturation \( S \), by applying the approximation

\[ e^x = 1 + x + x^2/2 + \ldots \]

and using only the first two terms. This gives us

Equation 2-22

\[ S = 1 + \frac{A}{r} - \frac{B}{r^3} \]
which is also known as the Köhler equation. The Köhler equation describes the two effects that determine the vapor pressure over an aqueous droplet. The Kelvin effect increases the vapor pressure over a droplet as compared to a flat surface but the Raoul effect could result in vapor pressure being higher or smaller than a flat surface, depending on the magnitude of the solute effect term $B/r^3$, relative to the curvature effect term, $A/r$. Plots of $S$ versus $r$ are known as Köhler curves. On a typical Köhler curve (see Figure 2-2), particles to the left of the maximum peak do not tend to shrink or grow, but stay in equilibrium. Once the peak saturation, $S^*$ is crossed, the particles become in an unstable equilibrium and tend to grow indefinitely, hence activating into cloud droplets.

Köhler’s theory described the effect of soluble solutes on the activation of CCN. Fletcher extended the theory to insoluble particles in 1958. Since then it has been identified that soluble gases, slightly soluble solutes, organic substances and insoluble material such as dust and carbonaceous material (soot) can also activate as CCN. The theoretical understanding of how organic particles, especially carbonaceous particles such as soot, can activate at atmospherically relevant relative humidities (super saturations), sometimes even smaller than those predicted by Köhler’s theory, is not well developed[Crouzet and Marlow, 1995; Lazaridis et al., 2000; Wexler and Ge, 1998]. However, due to the strong effect that activation of insoluble species in atmospheric aerosols, such as soot, can have on the chemical, physical properties of clouds, lifetimes of clouds and lifetimes of these species in the atmosphere, it is important to study their role in cloud formation.

2.4 Cirrus clouds

2.4.1 Importance of cirrus clouds

Upper tropospheric ice clouds, also known as cirrus clouds, appear at altitudes of 8 to 15 km, with recent studies indicating that as much as 40% of the earth is covered with cirrus at any given time. Cirrus clouds play an important role in the Earth’s climate by scattering and absorbing solar radiation given off by the Earth’s surface[Fu and Liou, 1993; IPCC, 1996; Liou, 1986; Pruppacher and Klett, 1997]. Clouds reflect sunlight back toward space, which reduces the solar energy available to the Earth (albedo effect), and at
the same time, also reduce radiative heat losses to space by trapping Earth's radiative heat (greenhouse effect). Which of these two opposing processes dominates depends on many parameters including cloud particle composition, cloud structure, cloud cover, and cloud location. Changes to any one of these parameters can have significant implications for climate.

Cirrus clouds also play an important role in the chemistry of the upper troposphere. Recent field and laboratory work has shown that cirrus clouds can perturb chlorine chemistry and contribute to ozone depletion[Borrmann et al., 1997a; Borrmann et al., 1997b; Borrmann et al., 1996; Jaegle et al., 2000; Kley et al., 1996; Solomon et al., 1997]. For example, multiphase sulfate chemistry in aqueous particles proceeds by the partitioning of SO$_2$(g) to the aqueous phase followed by oxidation to SO$_4^{2-}$(aq). This is the primary mechanism for the formation of acid rain around the world. However, if the aqueous particles freeze into crystalline particles, this oxidation pathway is blocked. Another example is N$_2$O$_5$ hydrolysis, which proceeds rapidly on aqueous (NH$_4$)$_2$SO$_4$ particles but only slowly on solid (NH$_4$)$_2$SO$_4$ particles.

Although cirrus clouds have a potentially large influence on the Earth's climate and chemistry, estimating the magnitude of that influence is complicated by the lack of understanding of how ice nucleates in cirrus clouds. Until recently, knowledge of the microphysics of cirrus ice clouds was quite limited but advances in laboratory and field instrumentation has made it possible for in-depth study of microphysical processes that lead to the formation of cirrus ice clouds. Understanding cirrus cloud formation requires an investigation into the phase transitions of partially or fully neutralized sulfuric/nitric acid particles.

2.4.2 Liquid-to-solid phase transitions:

Cirrus clouds form when tropospheric aqueous aerosols cool in rising air parcels, take up water and grow in size as the relative humidity (RH) increases, and eventually freeze as the temperature decreases on top of the rising air parcel[Jensen et al., 1994a; Jensen et al., 1994b; Pruppacher and Klett, 1997]. Nucleation plays a fundamental role in first order phase transitions such as precipitation, condensation or crystallization, where a
kinetic energy barrier is present. In the case of liquid to solid phase transitions, the aqueous aerosols super-cool before overcoming the kinetic energy barrier and freezing.

Nucleation of ice tropospheric aerosols can occur by two processes: Homogeneous and heterogeneous nucleation. Homogeneous nucleation refers to the spontaneous and stochastic nucleation of ice in super-cooled liquid aerosols without the presence of any foreign substrate[Detwiler, 1989; Heymsfield and Miloshevich, 1993; Jensen et al., 1996; Sassen, 1989; Sassen and Dodd, 1988]. The nucleation statistics, in this case, are Poisson type[Martin, 2000]. Heterogeneous nucleation, on the other hand, refers to the nucleation of ice on a foreign substrate, such as mineral dust, in contact with the aqueous medium. The presence of a solid substrate often reduces the free energy barrier for nucleation[Pruppacher and Klett, 1997; Seinfeld and Pandis, 1998; Vali, 1994], and heterogeneous nucleation usually occurs at lower saturation ratios than homogeneous nucleation, that is, at warmer temperatures or lower relative humidities. Until recently, homogeneous freezing of aqueous particles was considered to be the dominant formation mechanism of UT ice clouds. Consequently, homogeneous freezing of aqueous particles has been investigated extensively[Cziezo and Abbatt, 2001; Koop et al., 1999; Koop et al., 2000; Koop et al., 1998; Martin, 2000; Sassen, 1989; Sassen and Dodd, 1988; Vali, 1994]. Specifically, the freezing properties of binary and ternary solutions of (NH₄)₂SO₄, H₂SO₄, and H₂O have been investigated (on the basis of modeling results and field data, atmospheric particles are believed to contain these compounds). However, several recent studies have shown that heterogeneous nucleation may be an important mechanism for formation of ice clouds[DeMott et al., 1999; DeMott et al., 1997; Heymsfield and Miloshevich, 1995; Heymsfield et al., 1998; Jensen and Toon, 1992; Jensen and Toon, 1997; Jensen et al., 1998a; Jensen et al., 1998b; Martin, 2000]. The role of heterogeneous nucleation in cirrus clouds is the subject of renewed attention in laboratory and field studies.

2.4.2.1 Homogeneous Nucleation

Classical Nucleation Theory (CNT), as described above, can also be used to describe the freezing process as a reaction rate. The first step in the liquid to solid phase transition is the formation of small molecular clusters that resemble the solid crystal.
These molecular clusters are formed as a result of fluctuations in the ensemble and remain in equilibrium with the liquid solution. When the size of the molecular clusters exceeds a critical value, they grow spontaneously and the formation of critical size nuclei is called nucleation.

Similar to the CNT expression for gas-to-liquid condensation, an expression for the Gibbs free energy change is found for the formation of a solid nucleus in a liquid droplet:

\[
\Delta G_i = -\frac{4\pi r_i^3}{3\upsilon_{sol}} kT \ln S + 4\pi r_i^2 \sigma_{sl}
\]

The first term in the equation corresponds to the transfer of molecules from the liquid to the solid phase, and the second one to the formation of an interface. The cluster with the maximum \(\Delta G_i\) is called a critical nucleus and its properties are:

\[
r_i^* = \frac{2\sigma_{sl} \upsilon_{sol}}{kT \ln S}
\]

\[
i_i^* = \frac{32}{3} \pi \upsilon_{sol}^2 \left( \frac{\sigma_{sl}}{kT \ln S} \right)^3
\]

\[
\Delta G_i^* = \frac{16}{3} \pi \sigma_{sl}^3 \left( \frac{\upsilon_{sol}}{kT \ln S} \right)^2
\]

where \(r_i^*\) is the critical radius of the nucleus, \(i_i^*\) is the number of molecules in the critical nucleus and \(\Delta G_i^*\) is the free energy of formation of the critical nucleus.

\(\Delta G_i^*\) and \(i_i^*\) decrease with the increase in saturation ratio. A cluster, which has not yet reached the critical nucleus size, would fall apart because the cluster's free energy increases with the addition of molecules. However, once the critical cluster size is reached, it continues to grow. Hence, the formation of a critical nucleus represents the
effective energy barrier in the nucleation process, along with the energy required for the transfer of one molecule from the liquid to the solid. For aqueous systems where the transfer of molecules from the liquid to the solid phase is not impeded (non-viscous solutions), once a critical nucleus is formed, the entire particle would freeze almost instantaneously. Using this rationale, Turnbull and Fisher [Turnbull and Fisher, 1949] derived the following equation for the nucleation rate $J$:

**Equation 2-27**

$$J = \frac{n_{\text{eq}}}{h} \exp \left[ - \frac{(\Delta G_{\text{act}})}{kT} \right]$$

**Equation 2-28**

$$\Delta G_{\text{act}} = \Delta G^* + \Delta G_{\text{diff}}$$

where $n_{\text{eq}}$ is the concentration of the monomer in the liquid and $\Delta G_{\text{act}}$ is the total activation energy. As shown in Equation 2-28, $\Delta G_{\text{act}}$ has two parts: $\Delta G^*$ is the activation energy for the formation of the critical nucleus, and $\Delta G_{\text{diff}}$ is the activation energy for the diffusion of atoms of molecules across the liquid-solid interface. The above equation is
not valid for phase transitions that involve more than one component, since long-range diffusion has to be considered. However, in those cases, the equation can be applied if $\Delta G_{\text{diff}}$ is taken as the activation energy of the most slow-moving component. In such a case, the expression must be multiplied by the mole fraction of the precipitating component. $\Delta G^*$ decreases as the saturation ratio increases (decrease in temperature) and the interfacial energy decreases as the liquid becomes more ‘solid-like’. In contrast, $\Delta G_{\text{diff}}$ increases at lower temperature because diffusion is slower in more viscous liquids. Hence, according to the above equations, $J$ has a maximum as a function of temperature.

Classical nucleation theory describes the nucleation process in a simple way, but it has its shortcomings. CNT employs the capillarity approximation, which assumes that the small solid clusters have the same physical properties as the bulk. In addition, surface tension $\sigma_{\text{s}}$ is only defined at the equilibrium whereas nucleation usually occurs in supercooled liquids, away from equilibrium conditions. Similarly $\sigma_{\text{s}}$ and $\Delta G_{\text{diff}}$ are difficult to measure or estimate. Some of the modifications to the Classical nucleation theory are reviewed in Kelton[Kelton, 1991]. Figure 2-3a shows a schematic for homogeneous nucleation. As particles rise in the atmosphere in cloud updrafts, their equilibrium temperature drops and relative humidity increases. When the critical ice super-saturation is reached, ice nucleates in the aqueous particles.

2.4.2.2 Heterogeneous Nucleation

As mentioned above, the presence of certain structural singularities such as solid particles, crystallized salt cores and other undissolved impurities can cause nucleation of ice to occur at lower super saturations than homogeneous nucleation. The solid substrate provides an interface that facilitates the formation of the solid-like molecular clusters, and are called ice nuclei (IN). Hence, most effective heterogeneous ice nuclei are considered to be those that provide a better ‘molecular fit’ to the solid crystal[Martin, 2000]. The heterogeneous nucleation rate (defined as the number of nuclei formed per unit time and surface area of the substrate in contact with the liquid) depends on the shape, size, structure, morphology of the crystal, the contact angle between the impurity and the solid and the nature of defects and other nucleation centers found on the solid lattice[Turnbull, 1950; Walton, 1969].
The theoretical basis for quantifying heterogeneous nucleation is much less
certain than for homogeneous freezing. Theoretical descriptions would require
knowledge about the surface properties for the vast number of materials that can act as
ice nuclei in the troposphere. In general, the free energy of formation for heterogeneous
nucleation is written as:

Equation 2-29

$$\Delta G_{het} = \frac{4}{3} \pi r_i^2 f(m_{n_i}, x) \sigma_{ij}$$

where $r_i$ is the radius of the nucleus, $f(m_{n_i}, x)$ is a geometric factor[Pruppacher and Klett,
1997] that depends in the simplest case (spherical cap embryo on a curved and uniform
substrate) on the cosine of contact angle between the ice embryo and the substrate
nucleus $m_{n_i}$ and the ratio of the nucleus to ice embryo radius ($x=r_n/r_i$).

Equation 2-30

$$\frac{m_i}{n} = \cos \theta_i / n = \frac{\sigma_{sv} - \sigma_{sl}}{\alpha_{lv}}$$

where $\sigma's$ are the interfacial surface tensions ($s$ stands for substrate, $l$ for liquid phase). In
general, in the presence of efficient ice nuclei, the free energy for the formation of critical
nuclei (activation energy $\Delta G^*$) is lowered, compared to homogeneous nucleation. Figure
2-4 shows a schematic explaining the lowering of activation energy in the presence of an
efficient IN. The success of the classical nucleation theory in explaining the
heterogeneous nucleation process is surprisingly good since describing the interaction
between the nucleating crystal and the substrate by a single macroscopic parameter is at
best an approximation. The classical theory has several deficiencies, some of which have
been mentioned above, such as: (1) The macroscopic parameters such as contact angles,
interfacial surface tensions and density are bulk parameters whose applicability to sub-
micron nuclei has not been verified. For example, contact angle is typically measured on
flat surfaces or micron-sized particles, and it is not just a function of surface properties of
the substrate but also of temperature and super-saturation. (2) The theory assumes the
nucleating substrate to be energetically homogeneous, whereas, it is widely known that
the heterogeneous surface contains irregularities (steps, cracks, pores, chemical and
electrical inhomogeneities), which provide active sites for phase transitions to occur preferentially. (3) The theory assumes that surface diffusion of molecules on the substrate do not play an important role in the formation of a nucleus.

Ice nuclei can cause heterogeneous freezing in 4 different modes[Demott, 1995; Pruppacher and Klett, 1997]:

**Direct deposition mode:** direct adsorption of water vapor from the vapor phase onto the substrate surface where it is transformed into ice.

**Condensation freezing mode:** condensation of water vapor onto a particle that is at a temperature below freezing point of 0°C and at some point during the condensation process, the drop freezes.

**Contact mode:** the ice nuclei initiates freezing of ice at the moment it comes into contact with the super-cooled drop.

**Immersion mode:** the ice nuclei becomes fully immersed in a super cooled drop and eventually initiates freezing.

Figure 2-3b shows a schematic for the heterogeneous nucleation process for the formation of ice in atmospheric aerosols. In the immersion mode, ice nucleates in internally mixed aqueous particles when the critical ice super-saturation is reached. There
is a wide range of occurrence and activity of ice nuclei around the globe and the mode of nucleation varies with the type of ice nuclei, size and morphology of IN, and the meteorological conditions. Experiments by several researchers have led to an empirical equation that describes the number concentration of IN (\(N_{IN}\)) at any given temperature as a function of the ice super-saturation:

\[
N_{IN} = CS_{v,i}^b
\]

where \(S_{v,i}\) is the super-saturation in %, and \(C\) and \(b\) are 'constants' for a given air mass.

There are a wide variety of materials that can act as IN but their efficacy and role in heterogeneous nucleation of ice is not well understood. For example, clay minerals, carbonaceous particles, inorganic salts, metallic substrates, organic particles and biogenic material can act as IN. The number of IN in a total Aitken particle mass (AP) is typically quite small, approximately \(10^6\) for a total AP concentration of \(10^3\) cm\(^{-3}\)[Pruppacher and Klett, 1997]. Good ice nuclei are typically insoluble, are relatively large in size, have surface chemistry that favors the formation of extended hydrogen bond networks, provide crystallographic matches to ice lattice and contain active sites (chemical, morphological, electrical) to initiate nucleation[Finlayson-Pitts and Pitts Jr., 2000; Martin, 2000].
Chapter 3

HOMOGENEOUS NUCLEATION OF ICE IN NH$_4$NO$_3$/H$_2$O PARTICLES

3.1 Background

The occurrence and properties of cirrus clouds is one of the largest uncertain parameters in the global radiation budget and heterogeneous tropospheric chemistry. Cirrus ice clouds form when aqueous particles in the atmosphere cool with a rising air-mass and nucleate ice at high enough super saturations with respect to ice ($S^*_\text{ice}$). The nucleation of ice can occur via homogeneous or heterogeneous mechanisms, as described above. To date, significant efforts have been made to characterize the relative importance of the homogeneous and heterogeneous mechanisms of cirrus cloud formation, but no consensus has been reached yet[Demott, 1990; Demott, 1995; DeMott et al., 1997; DeMott et al., 1998; Heymsfield and Miloshevich, 1993; Heymsfield and Miloshevich, 1995; Heymsfield et al., 1998; Heymsfield and Sabin, 1989; Jensen and Toon, 1992; Jensen and Toon, 1994; Jensen and Toon, 1997; Jensen et al., 1998a; Jensen et al., 1996; Jensen et al., 1998b; Jensen et al., 1994b]. However, it is generally agreed that both mechanisms may dominate under different atmospheric conditions. Under polluted conditions, where the number density of ice nuclei (IN) is high and the cooling rate of
aerosol mass is low (small updraft velocity), heterogeneous nucleation may prevail[DeMott et al., 1997; DeMott et al., 1998; Jensen et al., 1998b; Jensen et al., 1994b; Lazaridis et al., 2000; Sassen and Benson, 2000; Vali, 1994]. In other conditions, homogeneous nucleation of ice may dominate the formation of cirrus ice clouds[Heymsfield and Miloshevich, 1993; Heymsfield and Miloshevich, 1995; Heymsfield et al., 1998; Jensen et al., 1996; Jensen et al., 1998b; Martin, 2000; Sassen, 1989; Sassen and Benson, 2000].

H$_2$SO$_4$ is, by far, the most abundant aerosol in the atmosphere but recent field measurements and modeling studies have shown that the presence of ammonia in the atmosphere can neutralize some of the acid. In addition to the sulfate, nitrate is also present in the atmosphere and measurements made during the SUCCESS field campaign[Dibb et al., 1998; Tabazadeh and Toon, 1998; Talbot et al., 1998] and in-situ single particle analysis[Murphy et al., 1998a; Murphy et al., 1998b] have shown that ammoniated nitrate may also be present in the atmospheric particle mass. While there have been many studies on the homogenous freezing of sulfate aerosols to date[Bertram et al., 2000; Bertram and Sloan, 1998; Chelf and Martin, 1999; Chelf and Martin, 2000; Chen et al., 2000; Koop et al., 1999; Koop et al., 1997a; Koop et al., 1997b; Koop et al., 2000; Koop et al., 1998; Martin, 1998; Martin, 2000; Prenni et al., 1998], there has only been one study reported[Cziczo and Abbatt, 2001] on the homogeneous freezing of binary NH$_4$NO$_3$-H$_2$O particles. These results need to be independently verified since there is disagreement in the literature on the results for homogeneous freezing presented for other particle compositions, especially for (NH$_4$)$_2$SO$_4$ and NH$_4$HSO$_4$, when different experimental techniques have been employed. Freezing measurements using optical microscopy and differential scanning calorimetry have observed larger super-cooling for aqueous particles before freezing occurred, as compared to measurements done using aerosol flow tube techniques. The reasons for the disagreement in critical ice nucleation temperatures, as a function of particle concentration, are not well-understood since classical nucleation theory predicts that the homogeneous nucleation rate for ice formation in aqueous particles should be extremely sensitive to temperature. In this chapter, the homogeneous freezing temperatures and critical ice super-saturations for binary NH$_4$NO$_3$-H$_2$O particles, using optical microscopy and differential scanning
calorimetry, are reported. We will also compare our results with existing literature data and discuss the ability of existing thermodynamic models to describe water activity and ice nucleation in super-cooled binary NH$_4$NO$_3$-H$_2$O particles.

3.2 Experimental

Homogeneous freezing of ice in binary NH$_4$NO$_3$-H$_2$O particles was investigated using optical microscopy and differential scanning calorimetry techniques. The same instrumentation, with slight modification, was also used to observe heterogeneous freezing of ice in aqueous (NH$_4$)$_2$SO$_4$ particles. The results for heterogeneous freezing of ice will be described in subsequent chapters of this thesis but the experimental apparatus is described here in detail.
3.2.1 Optical Microscope

The experimental set up consisted of an optical microscope (Zeiss Axioskop 20) equipped with a Linkam BCS 196 biological cold stage. This technique has been previously employed in our laboratory to study the homogeneous and heterogeneous freezing of ice in binary H2SO4-H2O, (NH4)2SO4-H2O and NH4HSO4-H2O particles[Bertram et al., 2000; Koop et al., 1999; Koop et al., 1998; Zuberi et al., 2001; Zuberi et al., 2002]. The microscope was used in the transmitted light (bright field) mode with long distance Zeiss objectives (magnification 10x, 40x and 50x) and variable Optovar lenses (additional magnification of 1.25x and 1.6x). Figure 3-1 illustrates the setup where the regular microstage has been replaced by the biological cold stage.
The BCS 196 cold stage is a closed system and can be sealed once the sample cell is placed on the temperature controlled silver block inside the cold stage. The sample can be moved in the x-y plane by a crucible holder connected to two manipulators attached to the outside of the stage. Cooling was achieved by flowing cold N₂ gas from a liquid N₂ reservoir through the silver block, and counter heating the silver block controlled the temperature. Linkam Temperature Controller allows for the heating and cooling rates to be varied between 0.01 and 130 K min⁻¹. The temperature calibration of the cooling block was performed in the range from 178.15 to 273.15 K by measuring the melting points of droplets and thin films of water (273.15 K), dodecane (253.55 K), octane (216.35 K), and toluene (178.15 K). All freezing experiments were performed at the rate of 10 K min⁻¹ unless specifically mentioned and the warming rate was 1 K min⁻¹.

Figure 3-3: Optical microscopy set-up
The sample cell is shown in Figure 3-2. It consists of a quartz crucible (15 mm in diameter, 300 mm base thickness) and an aluminum washer about 60 mm thick with an inner diameter of approximately 2 mm. This setup can be closed by a glass cover slide 150 mm thick. Two layers of Halocarbon grease provided the sealing between the crucible, the washer and the cover glass. The bottom surface of the cell was pretreated with an organosilane (AquaSil, Hampton Research Inc.) to produce a monomolecular hydrophobic surface layer that minimized heterogeneous effects from the glass surface. Previous studies in our laboratory have shown that this hydrophobic surface does not promote nucleation of ice. Particles, with sizes ranging from 10 to 55 µm, were deposited onto the hydrophobic surface with a nebulizer (Meinhard, TR30) and their concentrations were adjusted by exposing them to a fixed relative humidity. Aqueous aerosols were produced from a diluted aqueous solution by flowing N₂ gas through the nebulizer and the aerosol stream was directed at the crucible for 2-5 seconds to deposit the aerosols. For
heterogeneous freezing experiments with mineral dust and soot inclusions, the solid substrate was sprinkled onto the surface before depositing the aqueous particles. The composition of the aqueous particles could be changed by varying the total amount of water in the sample cell. After adjusting the particle composition, Halocarbon grease (Halocarbon Products, Series 28LT) was added to the cell and the cell was sealed. This resulted in the aqueous particles forming an emulsion, that is, each particle was surrounded by the Halocarbon grease. Isolating individual particles with grease minimized the mass transfer of water vapor from unfrozen particles to frozen particles, and thus, the concentration of individual particles remained constant throughout the experiment. To check the effect of Halocarbon grease on the freezing properties of aqueous particles, we measured the homogeneous freezing temperatures of aqueous particles with and without the grease present. These results were in agreement, within experimental uncertainty, providing evidence that Halocarbon grease does not affect the freezing of our aqueous particles.
During the course of an experiment, the particles were observed with a microscope via two focusing eyepieces and a video camera (Sony XC 75) connected to a videotape recorder. We could easily observe phase transitions in the particles due to a change in light scattering. For example, each individual particle would suddenly turn dark on freezing due to the difference in light scattering properties of liquid and crystalline particles. Furthermore, we could clearly distinguish between liquid particles,
completely solid particles, and liquid particles with solid inclusions. Consequently, we were able to determine homogeneous nucleation temperatures, dissolution temperatures, and heterogeneous nucleation temperatures of individual particles. Figure 3-3 is an illustration of the optical microscopy setup for freezing studies. The foreign particles in the sample cell would only be present for heterogeneous nucleation studies.

3.2.2 Differential Scanning Calorimetry

We also used differential scanning calorimetry (DSC) to conduct homogeneous and heterogeneous freezing experiments on aqueous-oil emulsions. DSC has been widely used for the characterization of both isothermal and non-isothermal crystallization behaviors. The experimental technique is described in detail elsewhere. [Chang et al., 1999; Koop et al., 1999] Briefly, emulsions were prepared by mixing 0.4 ml of an aqueous solution with 5.0 ml of lanolin-Halocarbon oil solution, and then shaking the resulting mixture with a high-speed mixer for approximately 5 minutes. The mixing speed and time were kept constant to maintain the distribution of aqueous particle sizes in all experiments. During experiments investigating heterogeneous nucleation of ice by soot particles, soot powder was added to the oil-aqueous mixture before high speed mixing to create internally mixed particles.

A commercial Perkin-Elmer DSC-7 instrument was used for the calorimetric experiments; it operates on the power-compensated null-balance principle (with temperature precision of ± 0.1 K) to ensure that both the sample and the reference cells have the same pre-determined rate of temperature change. This technique involved monitoring the differential energy required to keep both a sample (emulsion) and a reference (lanolin-Halocarbon oil mixture) at the same temperature, while the temperature was increased or decreased. The changes in the differential energy as a function of temperature were plotted as thermograms and peaks in the thermograms indicated phase transitions. The maximum sensitivity of the DSC-7 is around 0.1mcal s⁻¹ for a full-scale deflection. Normally, only a few milligrams of sample are required for each measurement. The aqueous particles in the emulsions had sizes ranging from 5 μm to 15 μm, as determined with the microscope. Figure 3-4 shows a schematic of the null-balance differential scanning calorimeter and the emulsions used for freezing studies.
As an example, Figure 3-5 illustrates the thermograms which are obtained upon freezing and melting of \( (\text{NH}_4\text{)}_2\text{SO}_4\cdot\text{H}_2\text{O} \) particles (in emulsion) of concentrations 10, 15.3 and 20.1 \% \( (\text{NH}_4\text{)}_2\text{SO}_4 \) by weight. The freezing and the melting peaks shift to colder temperatures as the concentration of the electrolyte increases in the particle solutions. In the case of homogeneous freezing, only one peak is observed during the cooling cycle and the area under the freezing peak corresponds to the percentage of aqueous particles in the solution that are frozen. In the heating thermograms, one or two peaks are observed, depending on the concentrations. At low concentrations, only one peak is observed, and this peak corresponds to melting at the ice-liquid equilibrium temperature. At higher concentrations (approximately >10 wt \%) two peaks are observed. The high temperature peak corresponds to melting at the ice-liquid equilibrium temperature and the low temperature peak corresponds to melting of the eutectic composition. The ice-liquid equilibrium temperatures and eutectic melting temperatures are determined from these heating thermograms by extrapolating these melting peaks to the thermogram base lines.

The operational temperature of the DSC ranges from 100 to 450 K. The cell temperature was calibrated using a Perkin-Elmer two-point calibration program with n-dodecane (Fischer Scientific, Purified Grade, mp 263.50 K) and cyclohexane GR (EM Science, solid-solid transition at 186.09K) as the two standards. All experiments were performed at the rate of 5 K min\(^{-1}\) unless specifically mentioned.

### 3.3 Results

Figure 3-6 shows our results for the homogeneous nucleation of ice in \( \text{NH}_4\text{NO}_3\cdot\text{H}_2\text{O} \), on a temperature-concentration phase diagram for binary \( \text{NH}_4\text{NO}_3\cdot\text{H}_2\text{O} \) mixture. The thick solid lines represent the equilibrium lines in the binary \( \text{NH}_4\text{NO}_3\cdot\text{H}_2\text{O} \) system. The open squares represent the median freezing temperatures obtained by optical microscopy as a function of the \( \text{NH}_4\text{NO}_3 \) concentration in the aqueous particles. The open and solid circles represent the homogeneous freezing temperatures for 10\% and 90\%, respectively, of the particles frozen in the DSC experiments. The fraction of particles frozen, as a function of freezing temperature, was obtained for each DSC run by integrating the area under the cooling thermograms. The thin solid line represents a best-fit curve through the optical microscopy results. As evident in Figure 3-5, our results for
homogeneous freezing of NH$_4$NO$_3$-H$_2$O particles as a function of particle concentration, obtained by two separate techniques of optical microscopy and DSC, are in excellent agreement.

3.4 Discussion

![Phase diagram for NH$_4$NO$_3$-H$_2$O binary system.](image)

Figure 3-6: Phase diagram for NH$_4$NO$_3$-H$_2$O binary system.

There has been only one published study on the homogeneous freezing of NH$_4$NO$_3$-H$_2$O, by Cziczo and Abbatt\cite{Cziczo2001}. Figure 3-7 shows the results obtained by Cziczo and Abbatt (solid triangles), as compared to our data (open squares, open and filled circles). Our results show a greater degree of super-cooling in NH$_4$NO$_3$-H$_2$O particles, before ice nucleation occurs. At this point we do not know the reasons for this disagreement but we suspect some systematic experimental artifact in
their system leads them to observe warmer freezing temperatures. Tabazadeh et al. [Tabazadeh et al., 2002a; Tabazadeh et al., 2002b] and Djikaev et al. [Djikaev et al., 2002] have proposed a surface freezing mechanism to explain a difference in homogeneous nucleation rates observed in different experimental techniques, but we do not think that a surface-freezing phenomenon explains the discrepancy. In their proposed mechanism, crystallization can take place on the surface of an aqueous particle, instead of inside the volume of the particle, in which case the surface free energies of suspended-in-air particles would be different from particles in our experiments that are either resting on a hydrophobic surface or are immersed in halocarbon grease or oil/lanolin mixtures. Depending on the relative surface free energies, the proposed mechanism suggests that the nucleation rates for suspended-in-air particles may be greater than in our experiments. To test this theory, we have conducted optical microscopy experiments where the particles are not included in an emulsion and considerable droplet surface is in
equilibrium with the surrounding air; however, even in such experiments we have not observed freezing of particles at warmer temperatures.

The following mathematical expression, which is based on emulsion experiments of NH₄F, NH₄Cl, NaCl and NaF aqueous solutions [Rasmussen, 1982] has been used in the past to predict the homogeneous freezing temperatures of (NH₄)₂SO₄-H₂O particles [Demott et al., 1994; Sassen and Dodd, 1988]:

Equation 3-1

\[ T_f = 235.15 - \lambda \Delta T_m \]

where \( T_f \) is an effective homogeneous freezing temperature for particles of size comparable to our particles, \( \Delta T_m \) is the equilibrium melting point depression for a specific salt concentration and the homogeneous freezing of pure water droplets is fixed at 235.15 K. \( \lambda \) is the sensitivity parameter. The dotted line in Figure 3-7 is the fit with \( \lambda = 1.0 \), and matches well with Cziczo and Abbatt data, whereas the thin solid line represents a value of \( \lambda = 1.6 \), and is a better fit to our data.

Koop et al. [Koop et al., 2000] have shown using a thermodynamic model that homogeneous freezing temperatures for aqueous atmospheric particles can be predicted using solely the water activity in the solutions, irrespective of the nature of solute dissolved in them. We have used this ‘water activity criterion’ to compare our experimental results with the predictions of the Koop et al. model. First, we calculated the water activity in NH₄NO₃-H₂O particles at the freezing temperatures using the thermodynamic model by Clegg et al. [Clegg et al., 1998] The water activity values, \( a_w \), were then used to calculate the freezing temperatures in particles similarly-sized as in our experiments using an expression for homogeneous nucleation rate, \( J \), given by Koop et al. [Koop et al., 2000]. We found that the Koop model predicted warmer temperatures than the observed freezing temperatures. It is important to note here that the Clegg model extrapolates thermodynamic data from experiments done on sub-saturated particles to colder temperatures and the extrapolation might not be correct.

The open diamonds in Figure 3-8 represent the freezing temperatures predicted by Koop et al.’s water activity criterion model, as a function of particle composition, if Clegg model [Clegg et al., 1998] is used to calculate water activities (far-right thin solid
Homogeneous nucleation of ice in NH₄NO₃/H₂O particles

line in Figure 3-8). In comparison, if the water activity in aqueous NH₄NO₃-H₂O particles is assumed to remain constant with temperature below the melting point (far-left thin solid line in figure 3-8), results shown by filled diamonds are obtained. In this case, the freezing temperatures are lower than the observed results. Our results fall in between the

Figure 3-8: Comparison between experimental data on NH₄NO₃-H₂O freezing and predictions by Koop et al.'s thermodynamic model. The thick solid line is the ice-liquid equilibrium line. The dotted lines are constant relative humidity contours. See text for details.
two predictions. Since the Clegg model is constrained by experimental data available only for sub-saturated solutions, and water activity in aqueous NH₄NO₃·H₂O solution probably does change slightly with temperature, we think the ‘actual’ water activity values in supersaturated NH₄NO₃·H₂O solution lie in between the two curves. Koop [Koop, 2003] has used the experimental data available above the melting temperatures to obtain water activities in supersaturated solutions via a linear extrapolation to lower temperatures (center thin solid line in figure 3-8). This extrapolation provides a good fit to freezing temperatures observed in our study (open triangles in Figure 3-8). The curve predicted by the Clegg model in Figure 3-8 (open diamonds) has a slight s-shape, which would not be expected from thermodynamic expressions for freezing point depression. The results from Cziczo and Abbatt also show a similar trend (filled triangles in figure 3-8), probably because they used the Clegg model to calibrate their compositions, and are not supported by Koop et al.'s water-activity-criterion model.
Figure 3-9: Critical ice supersaturations ($S_{ice}^*$) for homogeneous ice nucleation as a function of temperature for common atmospheric aqueous aerosols. The open circles represent the data for NH$_4$NO$_3$-H$_2$O particles.

As evident in figure 3-8, freezing temperatures predicted by Koop et al.’s water-activity-criterion model strongly depend on the extrapolated water activities in supersaturated solutions. The thin solid lines in Figure 3-8 are contours for constant relative humidity of 90% calculated using Clegg model, and as evident, applying different approximations results in large differences in calculated water activities. We think that in the absence of experimental data, the Clegg thermodynamic model does not provide a reasonable estimation of water activities in supersaturated NH$_4$NO$_3$-H$_2$O solutions. Further experimental work is needed to determine accurate water activities in super-cooled NH$_4$NO$_3$-H$_2$O solutions.

In order to better understand the applicability of our data to atmospheric conditions, we have calculated the critical super-saturations with respect to ice ($S_{ice}^*(T)$) that are required in our experiments for ice to nucleate in NH$_4$NO$_3$-H$_2$O particles. The critical ice saturation is defined by the following equation:
Homogeneous nucleation of ice in NH4NO3/H2O particles

Equation 3-2

\[ S_{\text{ice}}^*(T) = \frac{P_{\text{H}_2\text{O}}^*(T)}{P_{\text{ice}}(T)} \]

where \( S_{\text{ice}}^*(T) \) is the critical ice saturation at the freezing temperature \( T \), \( P_{\text{H}_2\text{O}}^*(T) \) is the equilibrium partial pressure of water over liquid NH4NO3-H2O particles at the freezing temperature, and \( P_{\text{ice}}(T) \) is the vapor pressure of ice at the freezing temperature. These critical ice saturation ratios can be calculated using the Clegg model [Clegg et al., 1998] or by using the calculated water activities (in which case \( S_{\text{ice}}^*(T) = aw/aw_{\text{ice}} \)).

The appropriately labeled curves in Figure 3-9 represent the \( S_{\text{ice}}^*(T) \) values that were reported for homogeneous freezing of (NH4)2SO4-H2O, NH4HSO4-H2O and H2SO4-H2O particles [Bertram et al., 2000; Koop et al., 1999; Koop et al., 2000; Koop et al., 1998]. These studies had shown that high super-saturations with respect to ice (1.5 to 1.7) were required for homogeneous nucleation to occur at upper tropospheric conditions. Our results are shown as open circles in Figures 3-9. The thick solid line is a best fit to our data. In the case of NH4NO3-H2O, higher ice saturations, 1.7 to 1.44 are required for homogeneous ice nucleation between temperatures of 200 and 235 K.

In conclusion, we have shown that a high degree of super saturation is required before ice crystallizes homogeneously in NH4NO3-H2O particles. We were not able to reproduce the homogeneous freezing data reported by Cziczo and Abbatt [Cziczo and Abbatt, 2001] and have found the freezing temperatures for NH4NO3-H2O particles to be lower than the previously reported data. We do not think the surface-freezing hypothesis presented in the literature explains the discrepancy between our results and previously published data. Homogeneous freezing is an important ice nucleation mechanism in the upper troposphere, especially in regions where ice nuclei concentrations are low and the cooling rates of the aqueous particles in cloud updrafts are large. Under these conditions, the homogeneous ice nucleation rate will determine the ice number density and the ice particle size, which affects cloud albedo and heterogeneous chemistry in the upper troposphere.
Chapter 4

HETEROGENEOUS NUCLEATION BY CRYSTALLIZED SALT CORES

As explained above, ice nucleation in atmospheric aerosols can occur via two mechanisms. While considerable effort has been made to characterize the homogeneous nucleation mechanism for the formation of ice in aqueous aerosols, little is known about ways in which the presence of a solid core inside an aqueous particle can trigger heterogeneous nucleation. While most aqueous particles in the atmosphere will contain insoluble solid cores, such as mineral dust and soot, some liquid \((\text{NH}_4)_2\text{SO}_4-\text{H}_2\text{SO}_4-\text{H}_2\text{O}\) particles in the upper troposphere may contain a solid core of crystallized salt\([\text{Martin}, 1998; \text{Tabazadeh and Toon}, 1998]\). For example, Tabazadeh and Toon\([\text{Tabazadeh and Toon}, 1998]\) have demonstrated using an equilibrium thermodynamic model \([\text{Clegg et al.}, 1998]\) and laboratory efflorescence data\([\text{Imre et al.}, 1997]\) that liquid \((\text{NH}_4)_2\text{SO}_4-\text{H}_2\text{SO}_4-\text{H}_2\text{O}\) particles in the upper troposphere may contain solid ammonium sulfate or letovicite in equilibrium with the liquid in the particles. The presence of these crystallized salts in UT aerosol particles may significantly reduce the temperatures and saturations required for ice formation, by providing sites for heterogeneous nucleation, and thus, changing the mode of formation of UT ice clouds from homogeneous nucleation to heterogeneous nucleation.
In this chapter, we investigate the possibility that ice nucleation via the immersion freezing mode may occur on (NH₄)₂SO₄ crystals. We prepared droplets containing a solid (NH₄)₂SO₄ crystalline core enclosed by a liquid (NH₄)₂SO₄-H₂O solution and determined the freezing temperatures of these droplets. In addition, we report conditions required for the immersion freezing of liquid NH₄HSO₄-H₂O particles with solid inclusions of letevicite and ice.

4.1 Experimental

Optical microscopy and differential scanning calorimetry were used to study the heterogeneous phase transitions in (NH₄)₂SO₄-H₂O and NH₄HSO₄-H₂O particles in the presence of immersed crystalline cores. The techniques are described in detail in Chapter 3.

4.1.1 Ammonium Sulfate Experiments

These experiments consisted of thermally cycling (NH₄)₂SO₄-H₂O particles with concentrations between 41.3 wt % and 44.6 wt %, and determining the phase transition temperatures of the particles during the thermal cycling. The composition and temperature of the particles during these experiments are shown in Figure 4-1a, and photographs of the particles taken during each stage of the temperature cycling experiments are shown in Figure 4-1b. The labels in the photographs in Figure 4-1b correspond to points A, B, C, D, and E in Figure 4-1a. The vertical and horizontal positions of the photographs indicate the temperature and experimental time at which they were taken during the course of the experiment.

First, the particles were cooled from room temperature (point A in Figure 4-1a) to 183 K (point B in Figure 4-1a) at the rate of 10 K min⁻¹. This resulted in ice and solid ammonium sulfate nucleating in the particles. The particles were then heated to a temperature above the (NH₄)₂SO₄–ice eutectic temperature (254.2 K, dash-dotted line in Figure 4-1a), but below the (NH₄)₂SO₄–liquid equilibrium line (point C in Figure 4-1a). Note that the temperature that corresponds to point C varied from experiment to experiment, but in all cases it was above the eutectic temperature and below the (NH₄)₂SO₄ dissolution temperature. At point C, each particle consisted of an internal
mixture of crystalline (NH₄)₂SO₄ in equilibrium with a liquid (NH₄)₂SO₄–H₂O solution with composition C*. The presence of the solid core is clearly visible in Figure 4-1b, photograph C. The identity of the crystalline core, (NH₄)₂SO₄, was determined from the

![Diagram](image)

Figure 4-1: (a) Temperature versus concentration phase diagram for (NH₄)₂SO₄–H₂O [Clegg, 1998]. The thin solid lines are the solid-liquid equilibrium curves for ice and (NH₄)₂SO₄ and the dash-dotted line represents the ice–(NH₄)₂SO₄ eutectic temperature. The thick solid line indicates the homogeneous ice freezing data reported by Bertram et al. [Bertram, 2000] for (NH₄)₂SO₄–H₂O particles. The solid triangles represent the homogeneous freezing events in our experiments. The dotted line represents the thermal history of the particles. The points A-E along the dotted line indicate the different stages (see text for detail) in the thermal cycle. While points A, B, and E also indicate the liquid composition of the particles, points C' and D' indicate the concentration of the liquid in equilibrium with solid (NH₄)₂SO₄ at stage C and D of the experiment. (b) Photographs taken at various stages of the thermal cycle as a function of time.
phase diagram. We will refer to the temperature at point C as the 'conditioning temperature' throughout the remainder of this paper. After the particles were held at the conditioning temperature for approximately 5 minutes, the cell was slowly cooled at 1 K min\(^{-1}\) until heterogeneous freezing of ice on solid (NH\(_4\))\(_2\)SO\(_4\) was observed (point D in Figure 4-1a). In all experiments, this slow cooling rate was chosen to allow the liquid in the particles to maintain equilibrium with solid (NH\(_4\))\(_2\)SO\(_4\) such that the liquid assumes its equilibrium composition D*. We have also performed heterogeneous freezing experiments at cooling rates of 3 K min\(^{-1}\) and 5 K min\(^{-1}\). The results obtained in these experiments agree with the results obtained at a cooling rate of 1 K min\(^{-1}\), within experimental uncertainty. These results provide evidence that the solid is always in equilibrium with the liquid when the particles are cooled at 1 K min\(^{-1}\). Finally, the temperature of the cell was increased at the rate of 1 K min\(^{-1}\) until the solid completely dissolved (point E in Figure 4-1a). From the dissolution temperatures, we calculated the compositions of the particles using a thermodynamic model[\textit{Clegg et al.}, 1998].

\subsection{4.1.2 Ammonium Bisulfate Experiments}

Temperature-cycling experiments were carried out on ammonium bisulfate particles with the following concentrations: 36 wt % (experiment i), 57 wt % (experiment ii) and 68 wt % (experiment iii). In each experiment, we thermally-cycled the particles in a manner similar to the ammonium sulfate experiments described above. The three vertical lines in Figure 4-2a represent the temperature and composition during each experiment. The diagram in Figure 4-2b illustrates the expected morphology of the particles at each stage of the temperature cycling experiments. First, the particles were cooled from room temperature (points Ai, Aii and Aiii on Figure 4-2a) to 183 K (points Bi, Bii and Biii on Figure 4-2a) at 10 K min\(^{-1}\) and held at 183 K for approximately 30 minutes. This resulted in homogeneous freezing of the liquid particles. Based on the thermodynamic model by Clegg et al.[\textit{Clegg et al.}, 1998], it was possible for three solid phases to be present in the particle at 183 K, but we were unable to determine if the third phase crystallized in the particles. The particles were then warmed at 1 K min\(^{-1}\) to a temperature below the solid-liquid coexistence line (points Ci, Cii and Ciii of Figure 4-2). At the conditioning temperatures (Ci, Cii, and Ciii) the particles contained both liquid
Figure 4-2: (a) Temperature versus concentration phase diagram for NH₄HSO₄–H₂O [Clegg, 1998]. The ice-freezing line represents the homogeneous freezing data for ice in NH₄HSO₄–H₂O reported by Koop et al. [Koop, 1999]. The points A–D indicate the different stages in the thermal cycle (see text for detail) for particles with three different concentrations i–iii (Note: only the two-dimensional phase diagram for NH₄HSO₄–H₂O is shown but once letovi cte crystallizes in solution, the solution becomes more acidic and leaves the two-dimensional space). (b) Pictorial illustration of the phases we expected to detect in NH₄HSO₄–H₂O particles at different stages of the thermal cycling experiments.

and solid in equilibrium. After being held at points Ci, Cii, and Ciii for approximately 5 minutes, the particles were then slowly cooled at 1 K min⁻¹ to 183 K (points Bi, Bii and Biii on Figure 4-2a), and then held at that temperature for approximately 60 minutes.

Finally, the cell was warmed at 1 K min⁻¹ to determine the concentrations from their equilibrium dissolution temperatures (points Di, Dii and Diii on Figure 4-2a). From these thermal-cycling experiments, we determined both the homogeneous freezing temperatures and heterogeneous freezing temperatures of the individual particles.
Figure 4-3: Percentage of drops frozen as a function of temperature for \((\text{NH}_4)_2\text{SO}_4-\text{H}_2\text{O}\) particles. The particles were cooled at 1K min\(^{-1}\). Solid circles are results from experiment with a conditioning temperature of 291.2 K, the solid triangles correspond to 263.2 K, and the solid squares correspond to a conditioning temperature of 255.2 K. The arrow indicates the expected homogeneous freezing temperature, 202.2 K, for homogeneous nucleation of a \((\text{NH}_4)_2\text{SO}_4-\text{H}_2\text{O}\) solution in equilibrium with a solid \((\text{NH}_4)_2\text{SO}_4\) core. This temperature was calculated as the point of intersection between the \((\text{NH}_4)_2\text{SO}_4\)-liquid equilibrium line and the homogeneous ice freezing line (see Figure 1a).

4.2 Results and Discussion

4.2.1 Ammonium Sulfate

The solid triangles in Figure 4-1a represent the homogeneous freezing temperatures determined with the microscope during several temperature cycling experiments. These freezing temperatures, which are in excellent agreement with the
homogeneous ice freezing results reported by Bertram et al. [Bertram et al., 2000] (thick solid line), did not vary from one experiment to the next, within the uncertainty of the measurements. In contrast, the heterogeneous ice freezing temperatures varied as a function of the conditioning temperature (see Figure 4-2a) used in the thermal cycling experiments.
Shown in Figure 4-3 are heterogeneous freezing temperatures from three separate experiments. The conditioning temperatures used in each experiment are indicated in the
figure. The higher the conditioning temperature the lower is the heterogeneous freezing temperature. We also determined heterogeneous freezing temperatures of aqueous (NH₄)₂SO₄-oil emulsions using differential scanning calorimetry. The emulsions were thermally cycled in the same manner as the microscope experiments. The temperatures at which the (NH₄)₂SO₄-H₂O particles froze heterogeneously in these DSC experiments also depended on the conditioning temperature 'C'. Figure 4-4 shows the median heterogeneous freezing temperatures as a function of the conditioning temperature, determined from the microscope and DSC experiments. The DSC and microscope results display a similar trend: heterogeneous freezing occurs at warm temperatures if the conditioning temperature is close to, but warmer than, the eutectic temperature.

What could be the physical reasons for these observations? Figure 4-5a shows the morphology of the solid when a conditioning temperature of 291.2 K was used, and Figure 4-5b shows the morphology when a conditioning temperature of 255.2 K was used. The photographs are of the same particle and since both photographs were taken at the same temperature (at 255.1 K), the mass of solid ammonium sulfate in the particle was the same in both cases. These figures show that the surface area of the solid changes drastically with the conditioning temperature. We have performed several heterogeneous freezing experiments and the same trend was observed in all cases: If the conditioning temperature was close to the dissolution temperature, but not above the (NH₄)₂SO₄-liquid equilibrium line, the structure of the solid in equilibrium with aqueous particle resembled Figure 4-5a. But if the conditioning temperature was close to the eutectic temperature, the particle resembled Figure 4-5b. For the intermediate case, the size of the solid crystals was between the size of the micro-crystals and the size of the large crystals. These

![Image of ammonium sulfate crystal](image)

**Figure 4-5:** Different morphologies of ammonium sulfate crystal in equilibrium with solution in aqueous particle.
Figure 4-6: α-β solid-solid phase transitions in ammonium sulfate. (a and b) mark the solid-solid phase transitions in ammonium sulfate. The arrows mark the different heterogeneous freezing temperatures based on different conditioning temperatures.

observations indicate that the trend in Figure 4-4 is due to the surface area and surface microstructure of the solid ammonium sulfate.

Using DSC, we were also able to observe the solid-solid transition of ammonium sulfate, α and β forms, as reported by Martin[Martin, 1998; Martin, 2000] and Bajpai et al.[Bajpai et al., 1990]. The α-β solid-solid phase transition is only possible in small droplets (< 50 μm) where high enough super-saturations are reached. However, since the
conditioning temperature was always warmer than the temperature for α-β ammonium sulfate solid-solid transition, we do not think the solid-solid phase transition affected heterogeneous freezing of the particles.

Figure 4-6 contains the thermograms which are obtained upon the cooling and warming cycles of (NH₄)₂SO₄–H₂O particles. The solid arrow show the different heterogeneous freezing temperatures that correspond to the different ‘C’ temperatures.

Figure 4-7: Schematic to explain the dependence of the surface area and morphology of solid (NH₄)₂SO₄ cores on the conditioning temperature in the thermal cycle. When the frozen particles (indicated by B) were warmed slightly above the eutectic, ice melted and left behind numerous micro-crystals of (NH₄)₂SO₄ in each particle (Cᵢ). When these particles were cooled without further warming, they readily froze because of the enhanced surface area available for nucleation (indicated by Dᵢ). However, when the temperature of these particles was raised further, to Cᵢ, the micro-crystals began to melt and eventually only one or two micro-crystals remained. Subsequent cooling of these particles resulted in only one or two large crystals in each particle, hence, minimizing the surface area of solid (NH₄)₂SO₄. These particles froze heterogeneously at Dᵢ.
that the particles were warmed to before cooling again. The peaks in the cooling
thermograms labeled ‘a’ at -53 °C correspond to the solid-solid transition between α and
β (NH₄)₂SO₄. These same peaks appear in the melting thermograms as well, labeled ‘b’,
but slightly shifted and at -50 °C. Figure 4-7 illustrates the surface area and surface
microstructure changes we observe with the microscope during the temperature cycling
experiments, and explains the relationship between the conditioning temperature and the
morphology of the solid ammonium sulfate. In all experiments, the (NH₄)₂SO₄–H₂O
particles were first cooled from room temperature (point A in Figure 4-7 to 183 K (point
B). Then the temperature was increased to slightly above the eutectic temperature. At this
point, ice melted and left behind numerous micro-crystals of ammonium sulfate in each
particle. What happened next, after the micro-crystals had been left behind, determined
the surface area of the solid, and hence, the heterogeneous freezing temperature. If these
(NH₄)₂SO₄–H₂O particles were subsequently cooled (from a low conditioning
temperature C₁ in Figure 4-7 without further warming, they readily froze (at temperature
D₁ in Figure 4-7). However, if the temperature of these particles was raised further to a
higher conditioning temperature, Cₓ, most of the micro-crystals dissolved, leaving behind
only one or two micro-crystals. As these particles were cooled, the micro-crystals grew in
size resulting in only one or two large crystals in each particle prior to heterogeneous
nucleation. Since the surface area of the solid ammonium sulfate was minimized in this
case, these particles super-cooled to a lower temperature and froze heterogeneously at a
temperature that corresponds to point Dₓ in Figure 4-7.

The above results show that the heterogeneous freezing temperature depends on
the thermal history of the crystals. In addition, these results show that there is a clear
trend between the surface area of the ammonium sulfate crystals and the heterogeneous
freezing temperature. This is consistent with classical nucleation theory, which predicts
that the heterogeneous freezing rate is proportional to the surface area[Pruppacher and
Klett, 1997]. From the microscope images we were able to determine the surface area of
the large crystals; however, we were unable to determine the surface area of the micro-
crystals. Consequently, we could not ascertain if the change in heterogeneous nucleation
temperature was due solely to a change in surface area. We have done calculations
(based on classical nucleation theory), which indicate that the required variation in
surface area between large crystals and micro-crystals would be beyond a physically reasonable quantity for surface area alone to be responsible for the variation in heterogeneous freezing temperatures. The difference in heterogeneous freezing temperatures shown in Figure 4-4 may also be due to the surface microstructure of the crystals (differences in surface defects of the crystals) since heterogeneous nucleation may occur predominately at surface defects such as cracks, steps, or dislocations. These surface defects may be enhanced on the micro-crystals that are produced at fast crystal growth rates due to the high super-saturations at point B. In comparison, when the crystals were prepared by growing one or two micro-crystals, the number of surface defects may be significantly reduced because the crystal growth rate is low, thus allowing for ion reorientation. Yet another possibility is that the heterogeneous freezing results may be due to pre-activation, which is a well-known phenomenon in heterogeneous nucleation theory[Pruppacher and Klett, 1997; Zhang et al., 1996]. Initial formation of solid ammonium sulfate in the presence of ice may modify the crystalline structure of (NH₄)₂SO₄ at the interface. This modified surface may have sites that closely match the ice lattice (activated sites). If the temperature is increased only slightly above the eutectic temperatures these activated sites may continue to exist on the solid ammonium sulfate surface, and as a result, heterogeneous freezing of ice may occur at much higher temperatures. On the other hand, the activated sites may not continue to exist if a conditioning temperature much warmer than the eutectic is used. Surface area, surface microstructure, and pre-activation of surface sites, are all possible explanations for our heterogeneous freezing results. All these possibilities are dependent on the thermal history of the particles.

In the experiments where only one or two large solid ammonium sulfate crystals were present in each particle, the average solid surface in each individual particle was 380 ± 260 μm². The median heterogeneous freezing temperature of these particles was 203.7 K. The temperature required for homogeneous nucleation of the ammonium sulfate solution that was in equilibrium with the ammonium sulfate crystals was calculated using the model by Clegg et al.[Clegg et al., 1998] and the homogeneous ice freezing curve determined by Bertram et al.[Bertram et al., 2000] (this corresponds to the intersection point of the (NH₄)₂SO₄-liquid line and the homogeneous ice-freezing line in Figure 4-1a).
Figure 4-8: Hypothetical atmospheric trajectory of an initially dry \((\text{NH}_4)_2\text{SO}_4\) crystal (shown as the dotted line) in a temperature vs. relative humidity phase diagram. The solid line is the ice saturation line and the dashed line represents the parameterization for homogeneous ice nucleation from liquid aqueous aerosols [Koop, 2000]. In the light shaded region ice is supersaturated whereas above the dashed curve (indicated as the dark shaded region) homogeneous ice nucleation will occur. The dash-dotted line indicates deliquescence relative humidity of \((\text{NH}_4)_2\text{SO}_4\) crystals as calculated using the model of Clegg et al. [Clegg, 1998]. For a detailed discussion, see text.

This freezing temperature, 202.2 K, is indicated in Figure 4-3 with an arrow. The calculated homogeneous ice freezing temperature is only slightly lower than the median heterogeneous ice freezing temperature of particles with one or two large \((\text{NH}_4)_2\text{SO}_4\) crystals, which indicates that a surface area of \(380 \pm 260 \mu\text{m}^2\) per particle does not significantly increase the rate of freezing of ammonium sulfate particles in our experiments.

We can use the experimental conditions to estimate an upper bound for the heterogeneous ice nucleation rate coefficient \(J_{\text{het}}\) on single \((\text{NH}_4)_2\text{SO}_4\) crystals. None of the 43 particles investigated crystallized at temperatures between 204 K and 254.2 K. To estimate an upper limit for \(J_{\text{het}}\) we take the minimum surface area of \(120 \mu\text{m}^2 \approx 380\) -
260 $\mu$m$^2$) and an observation time of 60 s at each 1 K temperature interval (the cooling rate was 1 K min$^{-1}$). Using Poisson statistics, Koop et al. (1997b) this yields an upper limit for $J_{\text{net}} \leq 1.5 \cdot 10^{-5}$ s$^{-1}$ $\mu$m$^{-2}$ with a confidence level of 99%.

Chen et al. (Chen et al., 2000) studied heterogeneous nucleation of ice by effloresced (NH$_4$)$_2$SO$_4$ particles. In these experiments the particles were completely crystalline until the deliquescence point was reached. In contrast, the particles in our experiments were always partially crystalline. Chen et al. (Chen et al., 2000) did not observe a decrease in the ice saturation ratio required for freezing in the effloresced (NH$_4$)$_2$SO$_4$ experiments when compared to ice formation in completely liquid (NH$_4$)$_2$SO$_4$ particles, indicating that crystalline (NH$_4$)$_2$SO$_4$ is a poor heterogeneous nuclei for ice. This result is consistent with the results we obtained when the solid was in the form of large crystals rather than micro-crystals.

The trajectories in our experiments (temperature and concentration histories) are not common in the atmosphere. Nevertheless, there is a range of atmospheric conditions for which our results are applicable.

The first situation is when the ratio of ammonia-to-sulfate in the atmospheric aerosol is exactly 2:1. In these cases, at low relative humidities, the particles will be completely dry ammonium sulfate. When the temperature decreases and the relative humidity increases, the particles will deliquesce and temporarily exist as a solid-liquid mixture. This is schematically illustrated in Figure 4-8. The dotted line shows a hypothetical atmospheric trajectory of an initially dry (NH$_4$)$_2$SO$_4$ crystal (at low relative humidity) in a rising air parcel. Upon increasing relative humidity, ice becomes supersaturated above the solid line and, hence, the dry (NH$_4$)$_2$SO$_4$ crystal can serve as ice nuclei in the deposition mode. If ice deposition nucleation does not occur, the (NH$_4$)$_2$SO$_4$ crystal will start to deliquesce once the appropriate deliquescence relative humidity value (dash-dotted line) is reached. At this point the (NH$_4$)$_2$SO$_4$ crystal will dissolve and intermediately form a crystalline core within a (NH$_4$)$_2$SO$_4$ solution. During the time it takes the crystal to fully deliquesce, ice nucleation via the immersion freezing mode may occur. If not, the particle will fully deliquesce and ice nucleation will only occur when the homogeneous ice nucleation limit (dashed line) is reached.
Our results might also be applicable when the ammonia-to-sulfate ratio in atmospheric particles is non-stoichiometric. In these cases, the particles can exist as partially crystalline ammonium sulfate, i.e. internally mixed liquid-solid particles, over a wide range of conditions in the atmosphere. This is likely the dominant situation in the atmosphere since the conditions required for forming perfectly stoichiometric particles are probably rare. For non-stoichiometric particles, the ammonium sulfate crystals will be in equilibrium with a non-stoichiometric solution. This is in contrast to our ammonium sulfate experiments where solid ammonium sulfate was always in equilibrium with a solution having a 2:1 ratio of ammonia-to-sulfate. Despite this fact, we suggest that the freezing temperatures of non-stoichiometric particles containing solid ammonium sulfate can be predicted based on the ice saturations required for heterogeneous freezing determined in our experiments. For example, we propose based on our freezing results that ice saturations only slightly larger than 1 are required to freeze non-stoichiometric particles containing microcrystals of ammonium sulfate. This assumes that the freezing temperatures can be predicted based on ice saturations regardless of the stoichiometry of the solution, which has been shown to be applicable for homogeneous ice nucleation from aqueous solutions [Koop et al., 2000].

We can estimate the fraction of \((\text{NH}_4)_2\text{SO}_4-\text{H}_2\text{O}\) particles (ammonia-to-sulfate ratio 2:1) in the atmosphere that will freeze heterogeneously during deliquescence using the \(J_{\text{het}}\) determined in our experiments. For this estimation we assume that during deliquescence each atmospheric particle consists of a 0.5 \(\mu\text{m}\) \((\text{NH}_4)_2\text{SO}_4\) crystal with a surface area of \(\sim 0.8 \mu\text{m}^2\) that is in equilibrium with the liquid (here we assume a spherical shape for the crystals, but similar results are obtained if we assume a cylindrical shape). Based on these assumptions, less than \(10^{-4}\) % of these aerosol particles would be frozen after 10 seconds, less than 0.7 % after 10 minutes, and less than 4.2 % after one hour at temperatures above 204 K. Since these estimates are based on upper limits for \(J_{\text{het}}\), the frozen aerosol fraction is likely to be significantly smaller than the values calculated here. The deliquescence process of an initially dry \((\text{NH}_4)_2\text{SO}_4\) may take between a few seconds and several minutes in the atmospheric situation depending on the rate at which the relative humidity increases and also on the absolute water vapor pressure. As a result, at maximum only a small fraction of the aerosols will have
nucleated ice during deliquescence. On the other hand, depending on whether microcrystals form upon efflorescence or not, the ice nucleation ability of (NH₄)₂SO₄ crystals might be significantly enhanced in the atmospheric situation. We conclude that it is important to understand the surface area and microstructure of atmospheric (NH₄)₂SO₄ crystals in order to evaluate their ability to act as heterogeneous ice nuclei.

4.2.2 Ammonium Bisulfate

The following concentrations were used in the ammonium bisulfate experiments: 36 wt %, 57 wt % and 68 wt % NH₄HSO₄. In all cases, the ammonium bisulfate particles did not freeze homogeneously while cooling from room temperature to 183 K. The particles did freeze, however, at 183 K, but even at this temperature it took approximately 30 minutes for all the particles to freeze.

In the experiments with 36 wt % NH₄HSO₄ particles, the liquid was in equilibrium with ice after cooling to B and subsequently warming to the conditioning temperature C(i) (see Figure 4-2). On cooling these particles to 183 K, heterogeneous freezing of a second solid phase was observed in less than 5 % of the particles (see Table 4-1). An additional 26 % of these particles froze when they were held at 183 K for approximately 60 minutes. The saturations with respect to sulfuric acid tetrahydrate (SAT), sulfuric acid hemi-hexahydrate (SAH), and letovicite in these liquid-solid particles at 183 K, calculated with a thermodynamic model[Clegg et al., 1998], are listed in Table 4-1.
Table 4-1: Results from heterogeneous freezing experiments on NH₄HSO₄–H₂O particles*

<table>
<thead>
<tr>
<th>Average concentration</th>
<th>No. of particles</th>
<th>No. frozen above 183 K</th>
<th>No. frozen at 183 K</th>
<th>S₁₈³K_ICE</th>
<th>S₁₈³K_SAT</th>
<th>S₁₈³K_SAH</th>
<th>S₁₈³K_LET</th>
</tr>
</thead>
<tbody>
<tr>
<td>i: 36 wt %</td>
<td>23</td>
<td>1</td>
<td>6</td>
<td>1.00</td>
<td>0.90</td>
<td>5.53</td>
<td>5252</td>
</tr>
<tr>
<td>ii: 57 wt %</td>
<td>12</td>
<td>2</td>
<td>5</td>
<td>1.57</td>
<td>0.12</td>
<td>0.87</td>
<td>1.00</td>
</tr>
<tr>
<td>iii: 68 wt %</td>
<td>10</td>
<td>0</td>
<td>2</td>
<td>1.04</td>
<td>2.22</td>
<td>40.84</td>
<td>1.00</td>
</tr>
</tbody>
</table>

*The experiments were conducted at three concentrations and the saturations with respect to the various solids at 183 K (S₁₈³K_SOLID) were calculated using the thermodynamic model of Clegg et al., H₂O(Clegg et al., 1998). The 36 wt % particles contained solid inclusions of ice while the 57 wt % and 68 wt % particles contained solid inclusions of letovicite. Less than 10 % of the total particles exhibited heterogeneous freezing at temperatures warmer than 183 K.

Since letovicite is highly supersaturated in these particles, the solid phase that nucleated on ice was probably letovicite. Even if a third solid phase crystallized in the particles, it would be below our detection limit. The saturations in Table 4-1, row 1, are lower limits to the saturations necessary for heterogeneous nucleation of a large fraction (>5 %) of NH₄HSO₄–H₂O particles with solid inclusions of ice at temperatures warmer than 183 K.

In the experiments with 57 wt % and 68 wt % NH₄HSO₄ particles, the liquid was in equilibrium with letovicite at the conditioning temperatures C(ii) and C(iii) in Figure 4-2. Only 9 % of these particles froze heterogeneously above 183 K (see Table 4-1). An additional 38 % froze when the particles were held at 183 K for approximately 60 minutes. The saturations with respect to ice, SAH and SAT in these solid-liquid particles at 183 K are given in Table 4-1 (rows 2 and 3). In the 57 wt % particles, ice was the solid that nucleated heterogeneously, as it was the only solid supersaturated in the liquid. Ice, SAT and SAH were all supersaturated in the 68 wt % experiments. Based on the results of Koop et al.[Koop et al., 1999], we believe that SAT is the solid that nucleated
heterogeneously on letovicite even though SAH has a higher super-saturation. We were unable to determine if a third solid nucleated in these particles.

We also used DSC to investigate heterogeneous freezing of 57.7 wt % NH₄HSO₄–H₂O particles. In these experiments, no heterogeneous freezing was detected above 183 K, which is consistent with the microscope results.

The solid in the NH₄HSO₄–H₂O experiments was always in the form of large crystals rather than micro-crystals. Producing micro-crystals in these experiments proved to be difficult because most of the micro-crystals were dissolved when the conditioning temperature was only 2 or 3 Kelvin above the eutectic. This can be explained by the slopes of the solid-liquid equilibrium curves for both ice and letovicite (see Figure 4-2). Because the solid-liquid equilibrium curves for both ice and letovicite are relatively flat, a slight increase in the conditioning temperature above the eutectic temperature results in significant dissolution of the crystalline solid (either ice or letovicite) in order to maintain the liquid-solid equilibrium. In contrast, the (NH₄)₂SO₄-liquid line is very steep, thus requiring only minor dissolution of (NH₄)₂SO₄ in order to maintain equilibrium.

Our heterogeneous freezing results show that when one or two large crystals of either ice or letovicite are present in NH₄HSO₄–H₂O particles, the freezing temperature does not deviate significantly from the homogeneous freezing temperature of NH₄HSO₄–H₂O particles. This is consistent with the (NH₄)₂SO₄–H₂O freezing results. To find out whether or not micro-crystals of letovicite or ice induces freezing at higher temperatures, as is the case with micro-crystals of (NH₄)₂SO₄, additional experiments will be required.

Our results show that the surface defects, micro-structure and morphology play an important role in determining the efficacy of an immersed solid core to nucleate ice via heterogeneous nucleation mechanism. The presence of micro-crystallites of solid ammonium sulfate act as potent ice nuclei in equilibrium with binary NH₄HSO₄–H₂O particles and may play an important role if they can exist in the atmosphere in equilibrium with aqueous mixed salt aerosols. Close to the boundaries between clouds and clear air, for example, aerosol particles and cloud droplets can undergo several thermal cycles, resulting in large temperature fluctuations and repeated freezing and melting events with the particles. This thermal history of the particles may be important in determining the nucleation mode for the formation of stable ice clouds. In addition,
Baker [Baker, 2001] has suggested that the thermal history of the particles, and the surface microstructure and morphology of the crystallized salt cores may be responsible for the phenomenon of 'ice multiplication' [Jacobson et al., 2000] at temperatures above -20 °C. Under such conditions, it is possible that heterogeneous freezing onto the solid inclusions in originally liquid droplets is responsible for the ice-particle concentrations far exceeding the typical concentrations of known ice nuclei. In light of this knowledge, more experiments need to be conducted to elucidate the role of crystallized ice cores in changing the microphysics of ice clouds in the upper troposphere.
Chapter 5

HETEROGENEOUS NUCLEATION OF ICE BY MINERAL DUST

Mineral dust has been identified as an abundant species in the troposphere that may act as efficient ice nuclei [Martin, 2000]. Mineral dust components include silicates, aluminum silicates, and iron oxides. Metal oxides and other crustal components are strong suspects for ice nucleation activity via immersion since they can provide well-ordered atomic arrays on their surfaces that can impart local order into nearby aqueous solutions. Mineral dust is found ubiquitously in the troposphere; it is largely produced in the Gobi and Saharan Deserts and becomes airborne in desert dust storms [Perry et al., 1997; Perry et al., 1999; Prospero, 1996; Uematsu et al., 1985]. Recent satellite images show wide seasonal and geographical dependencies of Saharan and Gobi Desert dusts [Husar et al., 1997]. Estimates of its global source strength range from 1,000 to 5,000 Mt/yr [Martin, 2000], with very high spatial and temporal variability. Figure 5-1 shows regions of the world where mineral dust is lifted into the
troposphere and transported. The dust particles produced under these conditions advect over long distances across the oceans and have been shown to become coated with sulfates and other electrolytes after they pass over polluted continental regions [Buseck and Posfai, 1999; Cantrell et al., 1997; Fan et al., 1996; Ganor et al., 1998; Niimura et al., 1998; Piketh et al., 1999; Posfai et al., 1994; Posfai et al., 1995]. Findeisen [Findeisen, 1938a; Findeisen, 1938b] first suggested in 1938, and Kumai [Kumai, 1951] and Isono [Isono, 1955] later confirmed, that solid particles suspended in the atmosphere, such as mineral dust might serve as ice nuclei. Since then several other researchers have investigated ice formation in pure and dilute water particles containing mineral dusts. However, these results generally do not apply to the upper troposphere since upper tropospheric aerosols are typically concentrated aqueous electrolyte solutions. Experimental data on ice formation in concentrated aqueous particles containing mineral dusts is crucial for improving models of upper tropospheric clouds.

We report here the conditions required for ice formation in aqueous ammonium sulfate particles containing kaolinite and montmorillonite. These two mineral dusts were chosen because they are considered to be the main components of tropospheric mineral
dusts [Hoffer, 1961; Mason, 1960; Vali, 1971]. \((\text{NH}_4)_2\text{SO}_4\cdot\text{H}_2\text{O}\) particles were chosen because they are representative of the aqueous particles found in the upper troposphere.

5.1 Experimental

We employed optical microscopy to investigate the heterogeneous freezing by mineral dusts. Two commercially available dusts, kaolinite (Fluka Chemika; purum, natural grade) and montmorillonite K10 (Aldrich Chemicals) were investigated in these studies without any purification or chemical alteration to the dusts.

The Optical microscopy technique, with slight modification, was used to study the role of mineral dust as ice nuclei in the immersion mode. Powdered dust was first sprinkled onto the pre-treated surface of the quartz cell and aqueous particles of \((\text{NH}_4)_2\text{SO}_4\) were then deposited onto the same surface using a nebulizer. Using this process, we were able to create 10-55 \(\mu\text{m}\)-sized aqueous particles that had numerous dust particles immersed in each aqueous particle, as determined by the microscope (referred to as liquid-dust particles from here on). After exposing these liquid-dust particles to a constant relative humidity in order to fix their aqueous composition, Halocarbon grease (Halocarbon Products, Series 28LT) was added to the cell and the cell was sealed.

![Figure 5-2: (a) Liquid ammonium sulfate particles with solid kaolinite inclusions. (b) Same particles with kaolinite inclusions, after freezing.](image)
Figure 5-3: Temperature vs concentration phase diagram for (NH$_4$)$_2$SO$_4$-H$_2$O-kaolinite. The thick solid lines are the solid-liquid equilibrium curves for ice and (NH$_4$)$_2$SO$_4$ and the ice-(NH$_4$)$_2$SO$_4$ eutectic temperatures. The thin solid line indicates the results reported by Bertram et al. [Bertram, 2000] for homogeneous freezing of ice (NH$_4$)$_2$SO$_4$-H$_2$O particles. The open circles represent our data for heterogeneous freezing of ice in individual (NH$_4$)$_2$SO$_4$-H$_2$O-kaolinite particles and the filled circles represent the median freezing temperatures calculated from the results of each set of experiments. The dashed line represents the equation $T_f = 242.21 - 1.7\Delta T_m$ (see text for detail).

During the course of an experiment, the particles were observed with a microscope via two focusing eyepieces and a video camera. We could easily observe freezing and melting of the particles in these experiments due to a change in light
scattering, since individual particles would suddenly turn dark on freezing. Figure 5-2a shows \((\text{NH}_4)_2\text{SO}_4\cdot\text{H}_2\text{O}\)-kaolinite particles before freezing. The contrast between the solid dust substrate and the aqueous solution is obvious. The frozen particles are shown in Figure 5-2b.

### 5.2 Results

Figures 5-3 and 5-4 show the phase diagram for the \((\text{NH}_4)_2\text{SO}_4\cdot\text{H}_2\text{O}\) system as well as our results for ice nucleation by kaolinite and montmorillonite, respectively. The thick solid lines are the solid-liquid equilibrium curves for ice and \((\text{NH}_4)_2\text{SO}_4\) and the ice- \((\text{NH}_4)_2\text{SO}_4\) eutectic temperatures, calculated with the thermodynamic model of Clegg et al.\cite{clegg1998}. The thin solid line indicates the results reported by Bertram et al.\cite{bertram2000} for homogeneous freezing of ice in \((\text{NH}_4)_2\text{SO}_4\cdot\text{H}_2\text{O}\) particles. The open circles in Figure 5-3 represent our data for heterogeneous freezing of ice in individual \((\text{NH}_4)_2\text{SO}_4\cdot\text{H}_2\text{O}\)-kaolinite particles and the filled squares represent the median freezing temperatures calculated from the results of each set of experiments. Similarly, the open circles in Figure 5-4 represent our data for heterogeneous freezing of ice in individual \((\text{NH}_4)_2\text{SO}_4\cdot\text{H}_2\text{O}\)-montmorillonite particles and the filled circles in Figure 5-4 represent the median freezing temperatures calculated from the results of each set of experiments. As observed in Figure 5-3 and 5-4, the presence of dust inclusions cause ice to nucleate in \((\text{NH}_4)_2\text{SO}_4\cdot\text{H}_2\text{O}\) particles at temperatures approximately 10 K warmer than those reported for homogeneous freezing of ice by Bertram et al.\cite{bertram2000}. We also conducted experiments (not shown here) without the presence of dust, and our results are in agreement with the homogeneous freezing data reported by Bertram et al.\cite{bertram2000}. This shows that the increased freezing temperature can be directly attributed to the presence of dust inclusions.
5.3 Discussion

The molecular composition of Kaolinite is $\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5$, with triclinic symmetry. Kaolin minerals are built up of layers of $\text{Si}_2\text{O}_5$ tetrahedra and $\text{Al}_2(\text{OH})_4$ octahedra, so that OH groups are exposed on one surface and silica on the other[\textit{Mason and Maybank}, 1958]. Electron microscopy results[\textit{Mason and Maybank}, 1958] show that kaolinite specimens contain a high proportion of well-formed pseudo-hexagonal plates. The diameter of individual crystalline particles of kaolinite is usually less than 0.5 $\mu\text{m}$[\textit{Mason and Maybank}, 1958]. Some previous studies of freezing of pure water droplets had predicted that due to the presence of dangling OH bonds on the surface, kaolinite can be an effective ice nucleus[\textit{Demott et al.}, 1994].

Montmorillonite, on the other hand, has a more complicated composition and a monoclinic symmetry. Montmorillonite, $5\text{Al}_2\text{O}_3.2\text{MgO}.24\text{SiO}_2.6\text{H}_2\text{O}$ (\text{Na}_2\text{O}, \text{CaO}), has a three layered structure with metal oxides sandwiched between two layers of silica. Montmorillonite is sometimes referred to as swelling clay since water molecules can strongly absorb between the layers to produce an expanded lattice. However, water is not strongly adsorbed on the surface of these crystals. Montmorillonite particles are usually smaller than kaolinite and are in the form of 0.002 to $>0.02$ $\mu\text{m}$ thin flakes with little evidence of crystallinity[\textit{Mason and Maybank}, 1958]. Some previous researchers had predicted that due to the hydrophobic nature of the silica groups exposed to the surface water molecules, montmorillonite may not be a good nucleus for ice[\textit{Demott et al.}, 1994; \textit{Mason and Maybank}, 1958]. Our results shown in Figure 5-5 suggest that the efficacy for kaolinite and montmorillonite to induce ice nucleation in (\text{NH}_4)_2\text{SO}_4-\text{H}_2\text{O} particles is similar.
Figure 5-4: Temperature vs concentration phase diagram for (NH₄)₂SO₄-H₂O-montmorillonite. The thick solid lines are the solid-liquid equilibrium curves for ice and (NH₄)₂SO₄ and the ice-(NH₄)₂SO₄ eutectic temperatures. The thin solid line indicates the results reported by Bertram et al. [Bertram, 2000] for homogeneous freezing of ice (NH₄)₂SO₄-H₂O particles. The open circles represent our data for heterogeneous freezing of ice in individual (NH₄)₂SO₄-H₂O-montmorillonite particles and the filled circles represent the median freezing temperatures calculated from each set of experiments. The dashed line represents the equation $T_f = 242.21 - 1.7\Delta T_m$ (see text for detail).
Figure 5-5: Increase in freezing temperature ($\Delta T$) vs aqueous concentration of particles when dust is present in the aqueous particles. $\Delta T = (T_{\text{heterogeneous freezing}} - T_{\text{homogeneous freezing}})$. The dotted line is only to guide the eye. The elevation of freezing temperature for particles with kaolinite and montmorillonite inclusions is similar.

Figure 5-5 also indicates that the elevation of the freezing temperature due to heterogeneous nucleation on the kaolinite and montmorillonite substrates is greater for more concentrated ($\text{NH}_4\text{SO}_4$-$\text{H}_2\text{O}$) particles. Figure 5-5 shows the difference in heterogeneous and homogeneous freezing temperatures for ice in ($\text{NH}_4\text{SO}_4$-$\text{H}_2\text{O}$) as a function of the concentration of the aqueous particles. The difference in ice freezing temperatures, with both kaolinite and montmorillonite, remained constant for particle concentrations less than approximately 27 wt % but increased for particle concentrations greater than 27 wt %. This difference in freezing temperatures varied from approximately 8 to 20 K over the range of concentrations studied. This result suggests that immersions
of dust will cause a larger effect on the freezing of ice in the atmosphere for the more concentrated particles.

The following mathematical expression, which is based on emulsion experiments of NH₄F, NH₄Cl, NaCl and NaF aqueous solutions[Rasmussen, 1982] has been used in the past to predict the homogeneous freezing temperatures of (NH₄)₂SO₄-H₂O particles[Demott et al., 1994; Sassen and Dodd, 1988]:

Equation 5-1

\[ T_f = 235.15 - 1.7\Delta T_m \]

where \( T_f \) is an effective homogeneous freezing temperature for particles of size comparable to our particles, \( \Delta T_m \) is the equilibrium melting point depression for a specific salt concentration and the homogeneous freezing of pure water droplets is fixed at 235.15 K. We used a similar expression to fit our median heterogeneous freezing temperatures of ice in (NH₄)₂SO₄-H₂O particles with dust immersions:

Equation 5-2

\[ T_f = 242.21 - 1.7\Delta T_m \]

The dashed curves in Figures 5-3 and 5-4 show the agreement of our median freezing data for both kaolinite and montmorillonite with this expression, with an error of \( \pm 3 \) K.

We did not investigate the freezing of pure water particles but we can extrapolate our combined freezing data for liquid-dust particles to 0 wt. % ammonium sulfate. As shown in Figures 5-3 and 5-4, we obtain 242.21 K as the ice nucleation temperature in pure water particles with dust immersions using a fourth order polynomial fit through our data points. Our results, obtained by extrapolation, are in reasonable agreement with previous studies[Hoffer, 1961; Fitter and Pruppacher, 1973].
Figure 5-6: Increase in freezing temperature ($\Delta T = T_{\text{heterogeneous}} - T_{\text{homogeneous}}$) as a function of surface area of kaolinite and montmorillonite. $\Delta T$ is a strong function of solid surface area for small values of surface area of kaolinite as immersion nuclei but plateaux off for larger values. Montmorillonite does not seem to present this trend.

In our experiments, we were unable to determine the exact surface area of the solid kaolinite and montmorillonite substrates that were present in our aqueous particles but we made an attempt to classify our particles into different bins according to the surface area as observed in the 2-dimensional optical image, assuming smooth surface for the particles (according to manufacturers, kaolinite had a surface area of 9 m$^2$g$^{-1}$ and montmorillonite, 220-270 m$^2$g$^{-1}$). Figure 5-6a shows the increase in freezing temperature, $\Delta T$, (as compared to homogeneous freezing temperature) as a function of the approximate surface area of kaolinite present in the particles (in arbitrary units). Similarly, Figure 5-6b shows the $\Delta T$ as a function of the approximate surface area of montmorillonite. As observed in Figure 5-6a, $\Delta T$ is sensitive to the surface area of
immersed kaolinite dust for smaller surface area of solid inclusions. The change in freezing temperature induced by the presence of the solid ice nuclei reaches a plateau for higher values of immersion nuclei surface area. This trend is not that pronounced for montmorillonite. We have performed a regression analysis and our results show a greater dependence of ΔT on kaolinite surface area than for montmorillonite. However, since most of our experiments were done with large amounts of dust inclusions and we do not have good resolution in determining the exact surface area of the solids in our particles, especially when the total surface area of solid immersions in the particles is small, we think our results present an upper limit to the heterogeneous nucleation activity induced by mineral dusts kaolinite and montmorillonite. Detailed experiments should be conducted to study if heterogeneous nucleation activity depends on surface area of dust inclusions for low concentrations of inclusions in particles or if a few active sites are enough to activate dust as a good ice nucleus as suggested by Karcher and Lohmann (Karcher and Lohmann, 2003). We also obtained scanning electron microscopy images of the kaolinite and montmorillonite dust that we used in our experiments, which indicated that kaolinite particles (see Figure 5-7a) were approximately ten times larger in diameter than the montmorillonite particles (see Figure 5-7b) but the total surface area of solids immersed in our aqueous particles was approximately the same in both set of experiments.
Hung et al. [Hung et al., 2003] have recently measured heterogeneous nucleation for ice with hematite and corundum mineral dusts as immersion ice-nuclei. They report $J$ values ranging from $10^{2.5}$ to $10^{5.5}$ depending on the conditions. We agree with their conclusion that our results represent an upper limit for heterogeneous nucleation rate constant $J$ for mineral dust as ice-nuclei. However, it is also possible that surface area is not the only controlling factor in heterogeneous nucleation. It is possible for cracks, cavities, steps and other defects, as well as impurities present on the insoluble substrate surface, to provide 'active' sites for nucleation. In the presence of such 'active' sites, nucleation would occur preferentially at these sites and the number of active sites present in the liquid-dust particle could have a greater impact on the heterogeneous freezing temperatures than just the geometric substrate surface area.

In order to better understand the applicability of our data to atmospheric conditions, we have calculated the critical super-saturations with respect to ice ($S_{\text{ice}}^\ast(T)$) that are required in our experiments for ice to nucleate in $(\text{NH}_4)_2\text{SO}_4$-H$_2$O-kaolinite and in $(\text{NH}_4)_2\text{SO}_4$-H$_2$O-montmorillonite particles. The critical ice saturation is defined by the following equation:

\begin{equation}
S_{\text{ice}}^\ast(T) = \frac{P_{\text{H}_2\text{O}}^\ast(T)}{P_{\text{ice}}(T)}
\end{equation}

where $S_{\text{ice}}^\ast(T)$ is the critical ice saturation at the freezing temperature $T$, $P_{\text{H}_2\text{O}}^\ast(T)$is the equilibrium partial pressure of water over liquid $(\text{NH}_4)_2\text{SO}_4$-H$_2$O and $(\text{NH}_4)_2\text{SO}_4$-H$_2$O-dust particles at the freezing temperature, and $P_{\text{ice}}(T)$ is the vapor pressure of ice at the freezing temperature.

The curves in Figure 5-8 represent the $S_{\text{ice}}^\ast(T)$ values that were required for homogeneous freezing of $(\text{NH}_4)_2\text{SO}_4$-H$_2$O, NH$_4$HSO$_4$-H$_2$O and H$_2$SO$_4$-H$_2$O particles[Bertram et al., 2000; Koop et al., 1999; Koop et al., 2000; Koop et al., 1998]. These studies had shown that high super-saturations with respect to ice (1.5 to 1.7) were required for homogeneous nucleation to occur at upper tropospheric conditions. In contrast, field measurements by Heymsfield and Milosevich[Heymsfield and Miloshevich, 1995] (thin solid line in Figure 5-8) suggested that the onset of upper tropospheric ice clouds occurs at lower ice super-saturations. Our results for
heterogeneous nucleation of ice on kaolinite and montmorillonite are shown in Figure 5.8 as open triangles and open circles, respectively. They indicate that for temperatures ranging from 239 K to 198 K, ice super-saturations between 1.35 and 1.51 are required for ice to nucleate heterogeneously in liquid-dust particles. These results are in better agreement with the field data than the homogeneous freezing results, but still deviate significantly at low temperatures.
Heterogeneous nucleation of ice by mineral dust

Figure 5-8: Critical ice saturations required for nucleation of ice in various aqueous aerosols. The dotted, dashed and dashed-dotted lines in the figure represent the $S_{ice}^*(T)$ values that were required for homogeneous freezing of ($\text{NH}_4$)$_2\text{SO}_4$-$\text{H}_2\text{O}$, $\text{NH}_4\text{HSO}_4$-$\text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4$-$\text{H}_2\text{O}$ particles, respectively. The thin solid line represents the field measurements by Heymsfield and Milosevich [Heymsfield, 1995]. Our results for heterogeneous nucleation of ice in ($\text{NH}_4$)$_2\text{SO}_4$-$\text{H}_2\text{O}$ particles on kaolinite and montmorillonite are shown as open triangles and open circles, respectively. The thick solid line is a least squares fit to the data points.

Table 5-1: Critical Ice Saturation for Freezing of ice in ($\text{NH}_4$)$_2\text{SO}_4$-$\text{H}_2\text{O}$ Particles with Solid Inclusions of Kaolinite and Montmorillonite Dusts as a Function of Temperature

<table>
<thead>
<tr>
<th>$S_{ice}^*(T)$</th>
<th>$A_0$</th>
<th>$A_1$</th>
<th>$A_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$-3.118 \times 10^{-5}$</td>
<td>$1.085 \times 10^{-2}$</td>
<td>$5.652 \times 10^{-1}$</td>
</tr>
</tbody>
</table>

$S_{ice}^*(T)$ can be calculated from $S_{ice}^*(T) = A_0 T^2 + A_1 T + A_2$, where $S_{ice}^*(T)$ is the critical ice saturation ratio and $T$ is the temperature (in K). These parameters are valid from 0 to 45 wt % ($\text{NH}_4$)$_2\text{SO}_4$. 

The thick solid line in Figure 5-8 is a least squares fit to the data points. The parameters that describe this curve are given in Table 5-1. A recent study [Koop et al., 2000] has suggested that homogeneous nucleation of ice from supercooled aqueous solutions is independent of the nature of the solute, and only depends on the supersaturation with respect to ice. Based on this, we suggest that our parameterization for the $S_{ice}(T)$ for heterogeneous nucleation by dust immersions can be used to predict freezing in other types of aqueous particles as well, and not just in (NH$_4$)$_2$SO$_4$-H$_2$O particles.

Koop et al. [Koop et al., 2000] suggested that not only can the homogeneous freezing rate be predicted based solely on supersaturation with respect to ice, or water activity ($aw$), but for a given $J$ value, the $\Delta aw$ ($\Delta aw=aw_{ice}-aw_{aq}$, where $aw_{aq}$ is water activity of the solution in equilibrium with ice) is a constant. It seems reasonable, based on these observations, to expect that the heterogeneous freezing temperature for a given surface area may also have a constant $\Delta aw$, but with a smaller $\Delta aw$. To test this, we have plotted our heterogeneous freezing results (median freezing temperatures) together with a constant $\Delta aw$ of 0.242 (see). The agreement with a constant $\Delta aw$ is not perfect. This could be due to variations in the mineral dust surface area and surface structure in our experiments. Alternatively, heterogeneous freezing results may not follow a constant $\Delta aw$. 
Figure 5-9: Heterogeneous freezing temperature vs water activity. The dashed line is the water activity at the melting temperature for aqueous solutions. The triangles represent the homogeneous freezing data for (NH₄)₂SO₄·H₂O particles reported by Bertram et al. [Bertram, 2000]. The filled circles represent our data for heterogeneous freezing of ice in (NH₄)₂SO₄·H₂O-kaolinite and the open circles represent our data for (NH₄)₂SO₄·H₂O-montmorillonite particles. The dashed-dotted line is the melting point curve shifted by Δa_w = 0.305 and the thick line is the melting point curve shifted by Δa_w = 0.242. See text for details.

In conclusion, our results show mineral dust, such as kaolinite and montmorillonite, can act as efficient ice nuclei in aqueous particles of varying ionic concentrations of NH₄⁺ and SO₄²⁻, causing aqueous (NH₄)₂SO₄·H₂O particles to freeze at warmer temperatures, and at lower ice super-saturations. This can lead to a reduction in ice crystal density in slow updraft cloud parcels, and hence also to a decrease in the net cloud albedo [DeMott et al., 1997; Kinne and Liou, 1989]. Even though our data are in better agreement with available field data than the homogeneous freezing results, it still deviates significantly at low temperatures. Further work is required to understand quantitatively the effects of increased surface area and surface defects that may provide
'active' sites for ice nucleation to occur. By considering the relationship between mineral aerosols and cloud properties over North Africa and the North Atlantic, using monthly mean observations of mineral aerosols and clouds over 16 years, Mahowald and Kiehl [Mahowald and Kiehl, 2003] have also recently shown that the mineral aerosols suppress precipitation in thin low altitude clouds and change cloud amounts in ice phase clouds. Due to the increased global transport of mineral aerosols, especially from North Africa, complicated feedbacks between mineral dust and global climate are expected. It is extremely important to understand the role of mineral dust in cloud processes, such as rain suppression and ice nucleation.
Chapter 6

HETEROGENEOUS NUCLEATION OF ICE BY SOOT

6.1 Background

Soot is found ubiquitously in the troposphere, especially in heavily populated urban areas\cite{Countess et al., 1980; Penner et al., 1992; Penner et al., 1993}, and has also been observed in numerous measurements in rural and remote atmospheres\cite{Wolff and Klimisch, 1982}. Soot is composed of two kinds of carbonaceous material in varying proportions: Elemental Carbon (EC) and Organic Carbon (OC). EC typically consists of black or graphitic carbon, while OC consists of a large number of hydrophobic or hydrophilic organic species. Typically, elemental carbon constitutes a few percent by mass of the total soot found in suspended sub-micrometer soot particles. Recent studies\cite{Cooke and Wilson, 1996; Lioussse et al., 1996; Penner et al., 1993} have estimated the world-wide anthropogenic emissions of black carbon to be in the range of 12-24 Tg yr\(^{-1}\). Relatively low black carbon concentrations, approximately 1 ng m\(^{-3}\), have been observed in the upper troposphere\cite{Pueschel et al., 1997} whereas the concentrations found in the Arctic are typically estimated at two orders of magnitude higher\cite{Cooke and Wilson, 1996; Lioussse et al., 1996}. However, significantly higher concentrations,
approximately 10 μg m⁻³, have been measured in cities with heavy traffic\cite{Hansen and Novakov, 1990; Heintzenberg and Charlson, 1996}. In addition, measurements, such as those of the arctic haze profiles\cite{Clarke et al., 2002; Hansen and Rosen, 1984; Rosen et al., 1981} have shown long-range transport of black carbon in the atmosphere, indicating a global movement and mixing of atmospheric soot.

Soot particles found in the troposphere are made up of fractal aggregates of primary spherical particles. While the size of soot particles vary considerably, the size of the individual spherules is typically between 30-60 nm. Individual spherules of the soot fractal aggregate are made of concentric crystallites in an onion-like structure. These crystallites have a small number of graphite-like planes presenting a relaxed structure with interplane spacing slightly larger than that in graphite. Several researchers have reported that the mean number densities of soot particles can range from 0.1-0.5 cm⁻³ and the BET surface area can vary from 150-450 m²/g\cite{Blake and Kato, 1995; Sheridan et al., 1994}.

The composition of soot, both elemental and organic components, has been the focus of many studies\cite{Chughtai et al., 1991; Goldstein and Siegmund, 1976; Graedel, 1986; Graedel and Crutzen, 1989; Graedel and Crutzen, 1993} and it has been found that the fuel composition, carbon/oxygen ratios, flame temperatures and in-situ processing greatly determine the chemical composition and physical properties of soot particles, such as surface morphology, micro-structure, porosity and hygroscopicity\cite{Ammann et al., 1998; Choi and Leu, 1997; Chughtai et al., 1991; Disselkamp et al., 2000a; Disselkamp et al., 2000b; Herring et al., 1996; Jacob, 2000; Kalberer et al., 1999a; Kalberer et al., 1999b; Kamm et al., 1999; Kotzick and Niessner, 1999; Kotzick et al., 1997; Lary et al., 1997; Lary et al., 1999; Longfellow et al., 1999; Ravishankara and Longfellow, 1999; Sergides et al., 1987; Sheridan et al., 1994; Smith and Chughtai, 1996; Smith and Chughtai, 1997; Smith et al., 1988; Williams et al., 1997; Winkler, 1988}. In addition, several researches have shown that reactions such as photo-oxidation or interaction with OH, O₃, NOₓ, HNO₃, H₂SO₄ and other radicals can lead to the formation of a variety of polar surface groups\cite{Decears et al., 2002; Kamens et al., 1988; Kamens et al., 1989; Kotzick and Niessner, 1999; Kotzick et al., 1997; Smith and Chughtai, 1995; Smith and Chughtai, 1997; Weingartner et al., 1997].
As described in previous chapters, ice clouds in the upper troposphere form via two mechanisms: homogeneous nucleation and heterogeneous nucleation. Heterogeneous nucleation by efficient ice nuclei can be the primary mode of ice nucleation in cirrus clouds that form in slow-updrafts. Field measurements [Heymsfield and Miloshevich, 1995; Heymsfield et al., 1998] in the upper troposphere have shown that heterogeneous nucleation may play an important role in ice nucleation, but not much is known yet about the properties of ice nuclei typically found in the upper troposphere. It is possible that soot, present ubiquitously in both rural and urban air masses, and especially in jet aircraft exhaust emissions, can act as potent ice nuclei. Recent aircraft exhaust plume calculations indicate that there are not enough particles for visible contrail formation unless soot can provide nucleation sites [Karcher et al., 1996; Schumann et al., 1996]. Recent studies by Karcher et al. [Karcher et al., 1996] and Demott et al. [Demott, 1990; DeMott et al., 1999] have shown that aircraft engine soot particles as small as 20-60 nm may be responsible for ice formation in aircraft contrail. Jet contrails may be viewed as artificial cirrus. Sulfur and soot emissions from aircraft are small compared with global sources, but in the altitude range (10-12 km), aircraft sources are estimated to be comparable to natural and anthropogenic sources [NASA, 1995]. Since soot is emitted directly into the upper troposphere by aircraft exhaust, in conjunction with other reactive gases and water vapor, it is hypothesized that rapid soot aging, especially in the presence of water soluble species such as H$_2$SO$_4$ and HNO$_3$, can cause soot to act as an efficient cloud condensation and ice nucleus.

The objective of this study is to investigate the formation of ice clouds on fresh and aged soot particles. For heterogeneous nucleation to be an efficient ice-formation mechanism, soot must serve as a suitable nucleus for ice nucleation. Due to the porous fractal structure, soot may be able to attract and retain water molecules in the micropores, and perhaps induce local order in water molecules to accelerate ice nucleation process. If soot does indeed act as an effective nucleus for ice formation, soot from anthropogenic sources may play an important role in the formation of cirrus clouds, thereby affecting the clouds' impact on the earth's radiation budget [Finlayson-Pitts and Pitts Jr., 2000; Fu and Liou, 1993; IPCC, 1996; Liou, 1986; Pruppacher and Klett, 1997; Seinfeld and Pandis, 1998] and the heterogeneous chemistry which occurs on these clouds [Borrmann
et al., 1997a; Börmann et al., 1996; Jaegle et al., 2000; Kley et al., 1996; Solomon et al., 1997]. Soot may also serve as a reactive surface for heterogeneous chemistry throughout the troposphere. With an atmospheric lifetime ranging from a few days to a few months, soot could play a major role in tropospheric chemistry.

In order to better understand the role of soot as efficient ice nuclei in the immersion mode, we have conducted laboratory measurements on heterogeneous ice nucleation in (NH$_4$)$_2$SO$_4$-H$_2$O particles in the presence of freshly generated, unoxidized soot as well as aged and treated soot.

6.2 Experimental

6.2.1 Optical Microscopy

We used optical microscopy to investigate heterogeneous nucleation of ice in (NH$_4$)$_2$SO$_4$-H$_2$O particles with soot as ice-nuclei (IN) in the immersion mode. The experimental apparatus is described earlier in detail. The only difference is in the manner in which soot was added to the particles so it formed an immersion in the aqueous particles. Briefly, fresh soot was either (a) directly collected onto the quartz crucible surface of the microscope cell or (b) collected onto an inverted glass funnel to be scratched off and sprinkled later on the cell surface. Ageing of the soot was performed in the laboratory by controlled exposure of the fresh soot to the appropriate ageing environment as described in Section 6.2.4. In case (a), aqueous ammonium sulfate particles were deposited on top of the soot surface with a nebulizer (Meinhard, TR30) which caused some of the soot to become immersed in the aqueous particle. In case (b), soot particles were sprinkled onto the surface of the quartz crucible. Aqueous ammonium sulfate particles were deposited afterwards with a nebulizer and soot became immersed in the aqueous particles. In both cases the internally mixed particles had a size distribution between 10 to 55 μm and their aqueous composition was adjusted by exposing them to a fixed relative humidity. After adjusting the particle composition, Halocarbon grease (Halocarbon Products, Series 28LT) was added to the cell and the cell was immediately sealed. This resulted in the formation of an emulsion, with individual aqueous particles surrounded by the Halocarbon grease.
6.2.2 Scanning Electron Microscopy and Energy Dispersed X-ray Spectroscopy

Off-line electron beam microscopy techniques offers a powerful method for single particle analysis, which involves deposition of particles onto a substrate that can be later probed by the electron beam for chemical, physical and morphological information. Transmission Electron Microscopy (TEM) has been extensively used to characterize the size, morphology internal structure of soot particles[Li et al., 2003a; Li et al., 2003b; Posfai et al., 1999; Posfai et al., 2003], and in this study, we have used computer controlled scanning electron microscopy (CCSEM) coupled with energy dispersed X-ray spectroscopy (EDX) to perform detailed analysis on size, morphology, structure and elemental composition of individual fresh and aged soot particles. In addition, as explained in the next chapter, environmental scanning electron microscopy (ESEM) was also successfully used to investigate the hydration behavior of fresh and aged soot particles as a function of relative humidity (RH).

Soot particles generated in laboratory were deposited onto TEM grids for analysis and processing. Gold (Au) TEM grids, coated with a thin (~50 nm) carbon film were used for this study (Ted Pella Inc. Carbon Type B on Au grid).

A FEI XL30 digital field mission gun Environmental Scanning Electron Microscope (ESEM) was used in this work (see Figure 6-1a). The microscope could be used in the ESEM mode with up to 10 torr of water vapor for hydration studies or under high vacuum SEM mode for chemical and morphological studies. The EDX spectrometer was an EDAX 136-10 with Si(li) detector of an active area of 30 mm² and ATW2 window, which allows X-ray detection from elements higher than beryllium (Z>4). “Genesis” hardware and software (EDAX, Inc) was used for Computer Controlled SEM/EDX analysis. The CCSEM/EDX analysis allows for automated analysis of individual particles on the sample area and has been used for detailed single particle analysis by other researchers[Krueger et al., 2003; Laskin et al., 2002]. During the analysis, the specified sample area on the grid was divided into several fields-of-view, and X-ray spectrum was taken of individual particles identified by a detector signal above a pre-set threshold value. In our study, a magnification of 8000x was used and imaging of particles was done in the transmitted electron mode (TED). The software was setup to
recognize features with equivalent circle diameter larger than 0.2 µm as particles. The X-ray spectra were acquired for 5s of clock time, at a beam voltage of 400-500 pA and an accelerating voltage of 20 kV. For quantification of the EDX results, a simple normalization method was used. The apparent particle composition was determined from the measured intensities of X-ray peaks relative to the theoretically calculated intensities of corresponding elements.

6.2.3 Soot-generation

Several previous studies on soot reactivity and hydration have used surrogate for soot, such carbon blacks. Soot particles have surface, structural and compositional characteristics demonstrably different from those of commonly-used surrogates for atmospheric soot. Major differences include soot reactivity, hydration, radiative properties, C,H,O content, surface functionalities, surface area, and porosity. In our measurements, we have used soot generated under environmental conditions so our results are more applicable to the atmosphere. Previous studies have indicated that the physical and chemical properties of soot depend on the chemical composition of the fuel and the temperature at which soot is collected[Choi and Leu, 1997; Chughtai et al., 1991; Disselkamp et al., 2000a; Disselkamp et al., 2000b; Jacob, 2000; Kamm et al., 1999; Kotzick and Niessner, 1999; Kotzick et al., 1997; Longfellow et al., 1999; Ravishankara and Longfellow, 1999; Sergides et al., 1987; Sheridan et al., 1994; Smith and Chughtai, 1996; Smith et al., 1988; Winkler, 1988]. However, Scanning Electron Microscopy analysis, coupled with Energy Dispersed X-ray Spectroscopy (SEM/EDX) has shown that methane soot closely resembles hexane soot in composition and morphology.(A. Laskin, 2003, personal communication) We used both methane and hexane as primary fuel for soot used in our experiments and have found the results to be similar. Methane soot was generated in a diffusion flame under relatively controlled (but not precise) fuel-air mixing ratios. A Bunsen flame with premixed methane/air mixture was used to produce soot under controlled flow and steady conditions. The fuel/air ratio was kept approximately constant by the use of mass-flow meters. Soot was collected at the top of the assembly on nylon filters, glass plates, quartz crucibles, or inverted funnels. Soot was produced under high fuel/air ratios, and at temperatures close to 1500°C. Our system
allowed us to vary the temperature at which we collected soot, from 45°C to 1500°C, by constant mixing of the soot plume with N₂/He gas mixture that has been pre-cooled by passing through a liquid N₂ bath. For the purpose of our studies, there was not much difference in composition, morphology and hydration behavior between soot collected at 45°C, 150°C and 1500°C and only high temperature soot was used for our studies. Figure 6-1b shows a photograph of the methane-soot generator with specific sections labeled.
Figure 6-1: (a) Environmental Scanning Electron Microscope used for size, morphology and atomic composition analysis of soot. (b) Soot generator using a fuel/air flame to produce soot.
Figure 6-2: Soot generation from n-hexane fuel. (a) TEM grids of 200 mesh copper, with 50 nm thick carbon coating were used to deposit soot particles for detailed compositional and morphological analysis. (b) Soot was generated in an open flame from liquid n-hexane fuel. An inverted glass funnel was used to constrict the flow of air and to collect the soot.

Figure 6-3: SEM images of n-hexane soot collected on TEM grids in the scattered electron mode (SE). The grids were Type B Cu 200-mesh with 50 nm thick carbon coating. (a) Secondary-electron image of soot particles on a grid. Notice the aggregated structure. (b) SEM image of a single soot particle at high magnification (16000x). Notice the individual spheres of diameter ~50-70 nm that constitute the aggregate fractal structure.

Hexane soot was produced in an open flame from liquid n-hexane fuel. Flow of air
Figure 6-4: (a) Energy-Dispersed X-ray spectrum of fresh n-hexane soot sample collected on TEM grids. (b) Size distribution of soot particles. The average diameter is the diameter of a circle with the same projection area as the soot particle.

was restricted by deploying an inverted glass funnel and soot was collected onto TEM grids or glass substrates at the end of the funnel. Figure 6-2a,b are photographs of the hexane-flame apparatus and an illustration of the TEM grids on which soot was deposited for compositional and morphological analysis. The fuel-air mixing ratios in the production of n-hexane soot were less controlled but no compositional or morphological differences were found in the soot produced. Hexane soot was analyzed for detailed morphology and chemical composition with CCSEM/EDX. Soot produced with n-hexane flame had the typical extensive fractal aggregate structure with each individual sphere of diameter approximately 50-70nm. Soot particles varied in size and shape, ranging from equivalent spherical particle diameters of 500nm to 2μm. Figure 6-3 shows SEM images (in secondary electron SE mode) of n-hexane soot used in our experiments. The extensive fractal structure is clearly visible in Figure 6-3a. For similar n-hexane soot particles other studies have reported the fractal dimension between 1.6 to 1.8. Figure 6-4a shows a typical EDX spectrum obtained for fresh hexane soot which indicates a very high carbon
content. Similar spectra were collected for over 200 individual soot particles and statistics show that average C atomic percent in the soot particles was C = 91 ± 3%. Average oxygen atomic percent in the soot particles was O = 5 ± 2%. This value is very similar to values for oxygen concentration reported by Ferry et al. [Ferry et al., 2002] for kerosene soot as O = 7.8% and by Popovitcheva and Trukhin [Popovitcheva et al., 2001] for combustor soot as O = 5%. The presence of oxygen in fresh n-hexane soot is largely attributed to the O-containing organic compounds found on the soot surface and the small peak of Si in the EDX spectra is attributed to the EDX detector itself which is Si-based. Van der Plas has reported that oxygen containing surface functional groups typically represent 90% of the total bound oxygen in soot [van der Plas, 1970].

In addition to determining the atomic composition of the soot, we have also calculated the median diameter of the soot particles generated for our study. Figure 6-4b shows a size distribution (diameter) of the soot particles analyzed with SEM. The equivalent spherical diameter means the diameter reported for soot is the diameter of a circle with the same projection area as the soot particle. Our laboratory-generated soot particles had a uniform and narrow size distribution, with an average diameter approximately 0.44 μm.

6.2.4 Oxidation

Fresh methane and n-hexane soot was aged or treated by different gas-phase exposure techniques to observe changes in the physico-chemical properties due to modification of the soot surface functional groups.

In the past few years, several studies have been conducted on the heterogeneous reactions that can occur due to reactive uptake of gas-phase species on soot surface. While soot concentrations in the troposphere are low compared to other aerosols, i.e. only a few percent of total aerosol mass loading, the extensive porous fractal structure of the soot particles provide surface area available for reactions similar to the total sulfate aerosol area, particularly under volcanically quiet conditions [Blake and Kato, 1995]. Hence, fast reactions during reactive uptake of aerosol gas-phase species on soot surfaces
could have a major impact on atmospheric chemistry[Hauglustaine et al., 1996; Lary et al., 1997].

In the past few years, several studies have shown that atmospheric trace species react with soot surfaces. FTIR studies have shown time-dependent formation of anhydride, phenolic, lactone, quinonoid, oxalic, and carboxylic groups on the soot surface during oxidizing reactions on soot, and simultaneous microgravimetric determination of water has indicated removal of hydrogen from the soot[Lary et al., 1999]. In addition, measurements have also shown the formation of volatile O₂, CO₂ and CO during the O₃- soot reaction, resulting in a loss of total carbon from the soot surface[Akhter et al., 1985; Chughtai et al., 1991; Kamm et al., 1999; Sergides et al., 1987; Smith et al., 1988]. While the initial O₃ reaction with soot is extremely fast, studies have shown the ozone decomposition rate to be a function of specific surface area, reaction time and temperature for very long exposure times[Kamm et al., 1999]. Rogaski et al.[Rogaski et al., 1997] have reported O₃ uptake coefficients on soot to be 1±0.7 x 10⁻³. In addition, even though the mass of a single soot particle increases in the initial reaction phase of O₃ due to the formation of carboxylic acid groups on the surface[Smith and Chughtai, 1996], Sergides et al.[Sergides et al., 1987] have reported a decrease in total particle size of ~40% and a decrease in surface area (due to reconstruction and collapse) of ~37% after prolonged (~300 hours) exposure to O₃.

Measurement of reactions of NO₂ and HNO₃ with soot with an FTIR have also shown the appearance of IR bands attributable to soot surface oxidation products and nitrogen containing species, e.g. R-NO₂, R-ONO₂, R-ONO, R-NNO₂. Kirchner et al.[Kirchner et al., 2000] have predicted the reactive uptake of these gases as a significant source of HONO in the troposphere. Choi and Leu[Choi and Leu, 1997] found that HNO₃ uptake coefficients were high and upon reaction with certain carbonaceous materials, HNO₃ was reduced to NO, NO₂ and H₂O. Rogaski et al.[Rogaski et al., 1997] report HNO₃ uptake coefficients of 0.038 ± 0.008. Kinetic studies of heterogeneous HNO₃-soot reaction have shown that the reaction is fast and surface limited, and the active sites for HNO₃ reactive uptake are not regenerated[Diselkamp et al., 2000a; Kirchner et al., 2000]. Kinoshita[Kinoshita, 1988] and Mahajan et al.[Mahajan et al., 1978] have reported that treatment of soot with HNO₃ is one of the most effective ways
to make carbon surface acidic. They show that the reaction of a carbonaceous surface with HNO₃ does not affect the physical morphology of the surface but only alters the surface functional groups.

While many studies have appeared in the literature on the oxidation and reactive uptake of O₃, HNO₃ and NOₓ on soot, not enough attention has been given to the reaction of tropospheric hydroxyl (OH) radical with soot constituents. A detailed discussion of OH chemistry in the troposphere is given by Logan et al. [Logan et al., 1981]. The primary source of OH is the photolysis of O₃ to produce an excited state of atomic oxygen, O¹D, which then reacts with water vapor to produce OH. Only 1% of the O¹D atoms produced react with H₂O while most are deactivated to the ground state O³P and recombine with O₂ to form O₃. It is estimated that the OH radical is consumed on a time scale of ~1 s by oxidation of a large number of reduced atmospheric species. It is expected that despite the variable concentrations of OH radicals (approximately 1.1±0.1 x 10^6 molecules cm⁻³ in free troposphere, with highest values in the tropical middle atmosphere [Krol et al., 1998; Miller et al., 1998; Prinn et al., 1992; Prinn et al., 2001; Prinn et al., 1994; Prinn et al., 2000]), fast reaction rates and high reaction probabilities of OH-soot reaction (personal communication, A. Ivanov, 2003) may result in rapid oxidation of surface organic functionalities, leading to faster ageing of ambient soot.

We have oxidized freshly generated laboratory soot using the following methods to observe changes in the ice-nucleation (this Chapter) and hydration behavior of soot (Chapter 7).

6.2.4.1 OH/O₃/UV Exposure in the Presence of H₂O

Two separate methods were used to expose methane and n-hexane soot to a mixture of OH/O₃/UV light in the presence of water vapor.

a) A mercury pen-ray lamp was used to generate OH/O₃ close to the soot surface by the reaction of O¹D with water vapor. Soot, directly deposited or spread out on a flat glass substrate, was placed in close proximity to the pen-ray lamp (less than 0.5 cm) in a setup where fresh air flow was maintained. The relative humidity was generally kept above 60% during the exposure. Soot was exposed to the resulting OH/O₃ mixture in the presence of UV light and H₂O for defined periods of time.
b) Soot was exposed to O$_3$/OH/UV in a flow tube at atmospheric pressure. O$_3$ was generated from a commercial O$_3$ generator (Jelight Company Inc. Model 600). The O$_3$ generator assembly houses a seven inch ozone producing double-bore lamp and can produce O$_3$ concentrations from parts per billion to 3100 parts per million. The concentration of O$_3$ inside the chamber was measured using an Ozone Monitor developed by Advanced Pollution Instruments Inc. (Model 450M). The concentration of O$_3$ inside the flow tube was approximately 15-25 ppm. OH was generated very close to the soot surface using a pulsed Q-switched Nd:YAG laser at 266 nm (Continuum Surelite). The pulse length of the laser was 10 nanoseconds and the repetition rate was 20 Hz. The maximum power or energy/pulse was less than 450 mJ. It is estimated that 10% conversion of O$_3$ to OH was achieved in the beam path. The relative humidity inside the flow cell was maintained above 60% at all times. The sample was exposed to the OH/O$_3$/UV light for defined periods of time.
Figure 6-5: (a) EDX spectra of a representative fresh n-hexane soot particle. (b) EDX spectra of the exact same particle after exposure to OH/O₃/UV light. The increase in the relative signal intensity for O is clearly visible.

We obtained EDX spectra of the soot samples before and after exposure to OH/O₃/UV light to observe any compositional changes to the soot surface. EDX spectra was taken of approximately 200 particles and a representative spectrum is shown in Figure 6-5. As illustrated in Figure 6-5b, the relative intensity of signal for O has increased, indicating a possible increase in Oxygen concentration in the soot. There is a slight increase in Si signal as well but this is entirely due to variation in Si signal coming from the detector itself. Statistically, the average relative O concentration (atomic percent) in the 200 analyzed soot particles increased from 2.6% to 3.1 % after exposure to OH/O₃/UV light. At the same time, the average relative C concentration decreased from 94.4% to 93.4%. While the exact concentrations derived from EDX spectra contain errors due to background signals (especially from
Figure 6-6: (a) TEM grids made of Cu and Au before exposure to concentrated \( \text{HNO}_3 \) vapor at room temperature. (b) severe oxidation of Cu grid indicates the high concentration of \( \text{HNO}_3 \) (g) in the sealed container. n-hexane soot was deposited on the Au grid and was exposed to this high concentration of \( \text{HNO}_3 \) (g).

the grids), the relative change in O and C concentrations for the same particles indicate a consistent change in the chemical composition.

6.2.4.2 Exposure to \( \text{HNO}_3 \)

Since concentrated aqueous \( \text{HNO}_3 \) has a considerably high vapor pressure at room temperature, a relatively simple apparatus was required to expose methane and n-hexane soot to high concentrations of \( \text{HNO}_3 \) vapor. Soot deposited on glass or TEM substrates was placed inside a sealed glass container with concentrated aqueous \( \text{HNO}_3 \) in a separate beaker inside the sealed glass container. The exposure was done at room temperature for defined periods of time and care was taken to ‘air’ the soot sample for a few hours after exposure to evaporate any condensed \( \text{HNO}_3 \) from the soot surface. Visual inspection showed no bulk condensation on the soot surface.

Figure 6-6 shows a photograph taken of two TEM grids before and after exposure to concentrated vapor of \( \text{HNO}_3 \) for 12 hours. The TEM grid on the left hand side is made of Cu-mesh while the grid on the right hand side is made of gold. n-hexane soot was deposited on the gold grid and was analyzed under SEM/EDX for assessing morphological and chemical changes in the soot particles due to \( \text{HNO}_3 \) exposure. As observed in Figure 6-6b, the Cu grid has been oxidized severely during the exposure, indicating the large concentration of \( \text{HNO}_3 \) vapor in the sealed glass container.
EDX spectra taken for over 200 particles show a marked increase in the O and N signals, indicating a chemical change in the soot particles after exposure to concentrated HNO₃ vapors for 12 hours. Statistically, the average N concentration (atomic percent) in the same soot particles increased from 1.4% to 1.5% after exposure. At the same time, the average O concentration (by mass) increased from 4.8% to 4.9%. While the exact concentrations derived from EDX spectra contain errors due to background signals (especially from the grids), the relative change in O and N concentrations for the same particles indicate a consistent change in the chemical composition. Figure 6-7 shows representative EDX spectra for the soot particles before and after exposure to HNO₃. Figure 6-7b clearly shows the increase in the relative O signals. The small N signal is masked by the C peak.
6.3 Results and discussion

Figure 6-8 shows our results for the heterogeneous nucleation of (NH₄)₂SO₄-H₂O particles with soot particles immersed inside the particles. The thick solid lines are the equilibrium liquid-solid lines obtained using a thermodynamic model[Clegg et al., 1998]. The thin solid line represents the homogeneous nucleation of ice results obtained in our laboratory[Bertram et al., 2000]. The open squares are results with unoxidized and untreated, freshly generated soot particles as immersion ice nuclei. The open circles and open triangles are the results with soot particles that have been pre-treated with exposure to OH/O₃/UV in the presence of water and to concentrated HNO₃ acid vapor for 12 hours, respectively. As evident in Figure 6-2, the presence of unoxidized or oxidized soot in immersion mode does not have an impact on the ice nucleation temperatures, or critical ice super-saturations, in (NH₄)₂SO₄-H₂O particles.

Gorbanov et al.[Gorbanov et al., 2001] have shown that oxidized soot particles in their experiments acted as potent ice nuclei even though their results contradicted with the Fletcher theory. We are unable to reproduce their results and suspect experimental artifacts or contamination as probable causes for the discrepancy. Demott et al.[Demott, 1990] had suggested that the ice nucleation activity of soot aerosols increases with particle size, but since our particles contain a large amount of soot immersed in aqueous solutions, they represent an upper limit for the amount of soot present in atmospheric aqueous particles. Demott et al.[DeMott et al., 1999] had shown that for small coatings of aqueous H₂SO₄ on soot, ice nucleated at relative humidities that suggest formation via homogeneous nucleation mechanism. They were able to observe heterogeneous nucleation of ice on soot surfaces only when multiple layers of aqueous H₂SO₄ were present on the soot particles and have interpreted it as an indication that the interaction of soot with high doses of aqueous H₂SO₄ increased the efficiency of soot to nucleate ice from aqueous particles. We have not performed experiments with significant presence (by mass) of aqueous H₂SO₄ but our results with soot exposed for an extended period of time to concentrated aqueous HNO₃ vapors show no active IN activity by the aged soot particles.

Ferry et al.[Ferry et al., 2002] have used Quasi-Elastic Neutron Scattering (QENS) technique to study the phase transitions and behavior of adsorbed water layers...
on kerosene soot under atmospheric conditions. Their spectra above and below the triple point of water $T_m$ describe the translational and rotational diffusion of water molecules adsorbed in 0.5 nm, 2 nm and $\geq 2.5$ nm soot micropores. They show that below the water triple point $T_m$, an appreciable amount of water exists in the soot micropores in liquid form, even when the temperature is reduced to the lowest temperatures found in the troposphere. They suggest that the depression in the freezing temperature may be related to the pore dimension since water confined in the micropores appeared to freeze only at temperatures below 200 K. For small micropore sizes (~2 nm), water confined in the pores may be unable to form a regular H-bond network that is necessary for ice crystallization. The results reported by Ferry et al. [Ferry et al., 2002] for ice nucleation in porous soot at the microscopic level are in general agreement with our results for ice-nucleation by soot in relatively larger aqueous particles. If the soot porous structure does
not facilitate the formation of ice, bulk aqueous \((\text{NH}_4)_2\text{SO}_4-\text{H}_2\text{O}\)-soot particles in our experiments would nucleate ice at the homogeneous nucleation temperatures of pure \((\text{NH}_4)_2\text{SO}_4-\text{H}_2\text{O}\) particles of similar aqueous composition.

Jensen and Toon [Jensen and Toon, 1997] used a classical theoretical approach to demonstrate that existing concentrations of soot particles acting as efficient ice-nuclei would lower ice crystal concentrations in cirrus, as compared to homogeneous freezing scenario. There is a considerable debate on the high value of contact parameter \(m_{\text{un}}\) that Jensen and Toon used [Jensen and Toon, 1997] \((m_{\text{un}} = 0.8)\) since Karcher et al. [Karcher et al., 1996] have reported a value of \(m_{\text{un}} = 0.57\) and Demott et al. [DeMott et al., 1997] have suggested that some soot aerosols could have a contact parameter \(m_{\text{un}} < 0.1\). Nevertheless, both studies have predicted that for low updraft and warmer clouds, soot can potentially play an important role in lowering the threshold humidity for the formation of cirrus clouds.

Our results show that freshly generated soot, and soot oxidized by exposure to \text{OH/}O_3/\text{UV} as well as by exposure to concentrated \text{HNO}_3 vapors, is not a good nucleus for ice in aqueous \((\text{NH}_4)_2\text{SO}_4-\text{H}_2\text{O}\) particles. Even though our EDX analysis of the changes in surface chemistry indicate a reactive uptake of gas-phase species in the oxidizing environments causing the surface functional groups to become oxidized and hydrophilic (see Chapter 7 for more detail on hydrophilicity of oxidized soot), the similar ice-nucleation activity of fresh and oxidized soot indicate that the ice-nucleation potential of soot may be determined by soot morphology rather than by surface chemistry. This conclusion is in agreement with our previous results obtained with crystallized salt cores and mineral dust as heterogeneous ice nuclei, where changes in surface morphology and microstructure had drastic effects on the ice-nucleating properties of the IN. More studies need to be conducted to study the ice-nucleating efficiency of diesel soot and aircraft-generated soot, as well as laboratory soot produced under different temperature and fuel/air mixing ratios. It is also possible that organics produced in engine exhaust, such as polycyclic aromatic hydrocarbons (PAHs) may condense on the soot particles and the reaction products of these organic species would result in generating active ice-nucleation centers on the soot surface. Ageing of porous soot, especially in the presence of high concentrations of \text{OH}, \text{O}_3, \text{H}_2\text{SO}_4, \text{HNO}_3 and trace gases such as \text{NO}_x, may alter physical
and chemical properties of soot significantly, which may lead to ice-nucleation activity by some soot particles.
Chapter 7

CHANGES IN HYDROPHILIC PROPERTIES OF SOOT

7.1 Introduction

Soot is found ubiquitously in the troposphere, especially in heavily populated urban areas [Countess et al., 1980; Penner et al., 1993], and has also been observed in numerous measurements in rural and remote atmospheres [Wolff and Klimisch, 1982]. In fact, since all combustion processes lead to the formation of soot, it is considered that between 10-50% of all tropospheric particulates are carbonaceous [Lary et al., 1999]. Soot is composed of two kinds of carbonaceous material in varying proportions: Elemental Carbon (EC) and Organic Carbon (OC). EC typically consists of black or graphitic carbon, while OC consists of a large number of hydrophobic or hydrophilic organic species. Most soot particles collected and evaluated during field campaigns have been found to contain black carbon cores with thick organic coatings and condensed volatile organic compounds (VOCs) [Buseck and Posfai, 1999; Karcher et al., 1996; Kuhlbusch et al., 1996; Kuhlbusch and Crutzen, 1995; Kuhlbusch et al., 1998; Li et al., 2003a; Li et al., 2003b; Miakelye et al., 1993; Parungo et al., 1992; Penner and Novakov, 1996; Petzold et al., 1999; Posfai et al., 1994; Posfai et al., 1999; Posfai et al., 2003]. Soot is directly
emitted into the atmosphere in particulate form as a result of anthropogenic activities, such as the combustion of fossil fuel and biomass burning, and can get coated with additional organic species via condensation of the byproducts of photo-oxidation of hydrocarbons. The composition of soot, both elemental and organic components, has been the focus of many studies [Chughtai et al., 1991; Decesari et al., 2002; Goldstein and Siegmund, 1976; Graedel, 1986; Seinfeld et al., 1999; Seinfeld and Pandis, 1998; Smith and Chughtai, 1995], and as explained in Chapter 6, it has been found that the fuel composition, carbon/oxygen ratios, flame temperatures, in-situ processing and condensation of VOCs greatly determine the chemical composition and physical properties of soot particles [Ammann et al., 1998; Choi and Leu, 1997; Chughtai et al., 1991; Dissanayake et al., 2000a; Dissanayake et al., 2000b; Herring et al., 1996; Jacob, 2000; Kalberer et al., 1999a; Kalberer et al., 1999b; Kamm et al., 1999; Kotzick and Niessner, 1999; Kotzick et al., 1997; Lary et al., 1997; Lary et al., 1999; Longfellow et al., 1999; Ravishankara and Longfellow, 1999; Sergides et al., 1987; Sheridan et al., 1994; Smith and Chughtai, 1996; Smith and Chughtai, 1997; Smith et al., 1988; Williams et al., 1997; Winkler, 1988].

As discussed in Chapter 6, high-resolution Transmission Electron Microscopy (TEM) studies have shown that soot particles found in the troposphere are made up of fractal aggregates of primary spherical particles. While the size of soot particles vary considerably, the size of the individual spherules is typically between 10-60 nm. Individual spherules of the soot fractal aggregate are made of concentric crystallites in an onion-like structure which have graphitic cores [Dalzell et al., 1970; Erickson et al., 1964; Hughes et al., 1999; Koylu et al., 1995; Parungo et al., 1992]. Typical size of the soot-aggregates can vary between 0.1 μm and 2 μm (see Figure 6-3). Several researchers have reported that the mean number densities of soot particles in the troposphere can range from 0.1-0.5 cm⁻³ [Blake and Kato, 1995; Sheridan et al., 1994]. Soot particles are extremely porous due to their extensive aggregate structure and can have surface/mass ratios of up of 1000 m²g⁻¹ [Donnet and Voet, 1976]. The microstructure of the soot particles, the fractal form of the aggregates, and the porous, spongy nature of soot leads to complex thermodynamic and chemical properties. The thermodynamic properties of water in confined spaces, such as the in the micropores of soot aggregates, can vary
considerably, depending on the hydrophilicity of the surface (contact angle) and the size of the micropores. Recently, Crouzet and Marlowe\cite{Crouzet and Marlowe, 1995} have shown using a simple theoretical model that soot-like aggregated spherules with contact angle less than 90° could exhibit an inverse Kelvin effect, where the vapor pressure of adsorbed water over a concave surface could be higher than that over a flat surface. Due to capillary condensation on a pair (or a group) of particles, condensation nucleation activation can occur at much lower super-saturations than the particles in isolation. Crouzet and Marlowe\cite{Crouzet and Marlowe, 1995} demonstrated that by considering aerosol particles with contact angles less than 90°, their theory predicts a stable liquid ring to exist in equilibrium at any sub-saturation level, and that a critical super-saturation can be defined for which the system starts unrestrained condensational growth (activation). For the case of soot, their theory extends the question if ageing of soot aggregates can lead to a change in surface chemical groups such that the phenomenological value of contact angle is reduced below 90°. If that is possible, soot may also behave as relatively hydrophilic particles, capable of activation as a CCN.

Due to the extremely hydrophobic nature of freshly generated soot particles, soot present in the atmosphere has generally been regarded as relatively inactive in cloud microphysics. Since atmospheric degradation (oxidative decomposition to form volatile organic compounds), washout and rainout are the primary mechanisms for the removal of
carbonaceous aerosols from the atmosphere, soot was generally assumed to exhibit long residence times in the troposphere. Initially, the presence of soot particles embedded in cloud droplets [McMurry et al., 1996] sampled during field measurements was explained by the presence of a coating of water-soluble inorganic compounds on the soot surface which would cause soot to be entrained in aqueous atmospheric particles [Hallett et al., 1989; Lammel and Novakov, 1995; Rogers et al., 1991; Weingartner et al., 1997]. However, since then several researchers have reported a direct interaction between water and soot, especially with atmospherically processed soot which is also referred to as aged soot [Choi and Leu, 1998; Dissanayake et al., 2000a; Dissanayake et al., 2000b; Ferry et al., 2002; Gerecke et al., 1998; Herring et al., 1996; Kalberer et al., 1999a; Kalberer et al., 1999b; Kamm et al., 1999; Kotzick and Niessner, 1999; Kotzick et al., 1997; Lary et al., 1999]. It is now thought that aged soot particles develop hydrophilic active centers on the soot surface which may exhibit strong attraction and retention of water molecules.

Researches have shown that reactive uptake of OH, O3, NOx, HNO3, H2SO4 and other radicals on soot surface can lead to the formation of polar surface groups and an increased affinity to adsorb water [Chughtai et al., 1996; Chughtai et al., 1999a; Chughtai et al., 1999b; Decesari et al., 2002; Kamens et al., 1988; Kamens et al., 1989; Kirchner et al., 2000; Kotzick and Niessner, 1999; Kotzick et al., 1997; Smith and Chughtai, 1995; Smith and Chughtai, 1997; Weingartner et al., 1997]. Some of the products formed during reactive uptake of O3, HNO3, OH and NO2 on soot surface were described in chapter 6. The increased hydrophilicity of oxidized soot particle surfaces, coupled with the complex thermodynamics exhibited by the microporous soot structure [Crouzet and Marlow, 1995; Lazaridis et al., 2000; Wexler and Ge, 1998], has sparked interest in understanding if soot that has been processed during its atmospheric interactions with reactive atmospheric gas-phase species can develop higher affinity for water molecules. If the ageing of soot in the atmosphere can lead to the increased hydrophilic behavior, activation of soot particles as CCN at critical super-saturations relevant to atmospheric conditions and increased entrainment of soot particles into existing liquid cloud particles would greatly affect the atmospheric life-time of soot and the microphysical and chemical properties of the clouds [Menon et al., 2002].
Rainout and washout are the two primary mechanisms for the wet removal of soot particles from the atmosphere[Kotzick et al., 1997; Schurath and Naumann, 1998]. Additionally it has been shown that while non-activated soot, incorporated into existing cloud droplets, will lead to a decrease in cloud albedo by absorbing radiation[Ackerman et al., 2000; Jacobson, 2001; Martins et al., 1998], soot activated as a CCN can lead to an increase in cloud albedo by changing the droplet size distribution towards smaller droplets[Breon et al., 2002; Twomey et al., 1984] (see Figure 7-1). In the presence of oxidized soot, the total number of CCN that can activate into cloud droplets would increase, resulting in a distribution of the condensable water vapor over more drops, leading to smaller droplet sizes, increased albedo, and decreased precipitation[Ackerman et al., 2000; Kaufman et al., 2002; Rosenfeld, 1999; Rosenfeld, 2000]. In both cases, the hydrophilicity of soot and soot's ability to attract and retain water molecules will have a large influence on the radiative properties of the clouds. Additionally, the interaction of soot particles with water has implications for heterogeneous atmospheric reactions, such as the wet oxidation of SO$_2$ and N$_2$O$_5$ hydrolysis[Brodzinsky et al., 1980; Harrison and Pio, 1983; Smith et al., 1989] and photodegradation of particle-associated polyhydrocarbons[McDow, 1995; McDow et al., 1995].

In this study, we present experimental investigations into the hydrophilic properties of fresh and aged soot, and discuss the effects of increased hydrophilicity due to oxidation on wet-deposition removal mechanism for soot in the atmosphere.

7.2 Experimental

7.2.1 Soot preparation

Soot was generated using the schemes described in Chapter 6. Methane and n-hexane soot was used in our study.

7.2.2 Oxidation

The oxidation procedures, described in detail in chapter 6, were employed to age freshly produced laboratory soot. While experiments were performed at various exposure levels and times, it was observed that for exposure times used in our experiments, the
Changes in hydrophilic properties of soot 113

cchange in hydrophilic behavior was significant for small exposures and probably reached a plateau very rapidly. This observation is in reasonable agreement with previous studies\cite{Choi and Leu, 1998; Disselkamp et al., 2000a; Grassian, 2002; Kirchner et al., 2000; Prince et al., 2002; Tabor et al., 1994} that indicated the reactive uptake of O$_3$ and HNO$_3$ to be surface-limited and very fast.

7.2.3 Quartz Crystal Microbalance

Quartz Crystal Microbalance utilizes the piezoelectric property of crystals that do not possess a center of symmetry. Curie brothers were the first to observe the phenomenon of piezoelectricity, demonstrating that when some crystals were compressed in particular directions, an electrical potential proportional to the applied pressure developed between the deformed surfaces of the crystal. By the end of the century, the converse of the effect was also observed. Certain crystals, such as quartz, when cut in the form of a disc, oscillate with a fundamental frequency when an oscillating AC voltage is applied to electrodes attached to the two flat surfaces of the crystal. Over time, this technique and the theory behind it was refined and now quartz crystals are used frequently as resonators whose oscillation in the shear-mode depends on the applied AC voltage.

Sauerbrey in late 1950's showed that a film attached to the electrodes of a piezoelectric crystal, such as an AT-cut quartz crystal, causes a decrease in the resonance frequency that is proportional to the mass of the film. Hence, for films that covered an electrode surface evenly and weighed much less than the mass of the crystal, the change in frequency can be expressed as

\begin{equation}
\Delta f = \frac{2f_0^2}{\rho_q v_q} \Delta m = -\frac{f_0}{\rho_q t_q} \Delta m = -C \Delta m
\end{equation}

where $\rho_q$ and $v_q$ are the specific density and the shear wave velocity in quartz, respectively, $t_q$ is the thickness of the quartz plate, and $\Delta m$ is the mass of the solid film. It is however, important for the vibrations in the applied film to couple well with the oscillating crystal. For viscous films, the linear relationship breaks down and theoretical treatments have been developed to understand the coupled motions of a fluid on a crystal.
surface. The linear, proportional change in resonant frequency and the mass of the film has been the basis of using the piezoelectric quartz resonator as a microbalance [Rodahl and Kasemo, 1996]. Since the crystal commonly used for this purpose is quartz, it is also called a quartz crystal microbalance (QCM). We have used a QCM set-up to measure the relative uptake of water as a function of relative humidity on soot surfaces that were evenly coated on the gold electrodes.

We employed a 10MHz, AT cut quartz crystal microbalance in our experiments (Maxtek, Inc.). More details on the instrument and the holder assembly for controlled relative humidity measurements are given in Maxtek catalogue. 1-inch diameter crystals were used in our studies with polished vapor-deposited gold plates serving as electrode surfaces. A Maxtek Phase Lock Oscillator (PLO-10) was used to track the frequency of heavily damped crystals, and its phase-lock mechanism, which utilized an internal Voltage Controlled Oscillator to keep the phase difference between the crystal voltage and current at zero, allowed us to monitor the change in oscillation frequency as well as the conductance of the crystal. The use of a 10MHz crystal with a 0.1Hz resolution allows a detection limit of less than 0.5 ngcm\(^{-2}\) in mass, but in practice, we were able to detect mass changes at less than 0.1 monolayers of water adsorbed on gold surfaces. Soot was deposited on the crystals directly, as a thin, evenly spread layer on the top crystal surface.

### 7.2.4 Light Reflectometry

A unique light-based technique was developed to detect the activation of soot surfaces under supersaturated conditions. The technique relies on detecting the abrupt change in reflected light from a laser beam focused onto a soot sample, at a constant angle, when bulk water condenses on top of the soot surface. A variation of this technique is also used in dew-point hygrometers which utilize the reflective properties of a shiny cooled glass surface, coupled to a feedback loop, to measure the exact dew-point and frost-point of a volume of flowing air. Similarly, a more complicated technique utilizes the similar principle, but employing parallel or elliptically polarized light to detect small changes in surface refractive index profile, and hence calculating the thickness of absorbed layers on specularly reflective surfaces.
Figure 7-2: A schematic of the Teflon flow-cell used in light reflectometry studies.

The experimental setup consisted of a low-power 632.8 nm He-Ne laser that was focused at a constant angle onto a vertically supported glass slide coated with soot. The reflected light from the microscopically corrugated soot surface was focused onto a photodiode operating in the reverse-bias mode. The laser beam was focused and collimated using a combination of lenses. Since the flow cell had a finite depth (~3 mm), it was possible for us to prevent the reflected light from the top glass surface from entering the detector.

Soot was deposited onto a thin glass microscope cover-slide that was then attached as the bottom surface of a custom-designed Teflon flow-cell using Halocarbon grease. The cell was sealed on the top with another glass microscope slide and Halocarbon grease. Figure 7-2 shows a design of the sealed flow-cell through which a continuous flow of pre-determined mixture of wet and dry He was maintained at 150 SCCM using mass flow meters. The bottom surface of the sealed flow-cell was brought into close thermal contact with the temperature-controlled silver block of a Linkam biological cooling stage (BCS 196) with the help of screwed-on clamps. The cold stage was temperature-controlled electronically with the help of cold N₂ gas and heaters with a precision of ± 0.1 K and at cooling rates varying between 0.01 and 10 K. Varying the temperature of the silver block controlled the relative humidity inside the flow cell. The
temperature of the soot surface was within ± 0.1 K of the temperature recorded by the Pt-
resistor thermometer embedded inside the silver block.

![Diagram of laser reflectometry setup]

Figure 7-3: A schematic of the Laser reflectometry setup. Data acquisition was automated using a Labview interface.

The temperature readout on the Linkam display and the voltage registered by the photodiode as a measure of laser intensity was recorded digitally using a program created in Labview software environment. Figure 7-3 shows a schematic of the reflectometry setup. The entire setup was placed onto an optical table for optical stability and in a dark room to prevent interference from stray light.

Soot has an aggregated, granular structure and due to its dark color and microscopically corrugated surface, it scattered most of the incident laser light under subsaturation conditions (RH < 100%). In the course of each run, the system was first equilibrated at approximately 60% RH and then, while keeping the flows of He/H₂O constant, the temperature of the Linkam stage was cooled at a fixed rate of 0.1K/min. The decrease in temperature resulted in a proportional increase in ambient relative humidity inside the flow cell. As the RH slowly increased, the voltage signal from the photodiode was monitored. A sharp, abrupt change in the light intensity was recorded when bulk
water condensed on top of the soot surface due to the increased reflectance from the multi-layer water surface that formed on top of soot. We labeled this event as activation and the ambient conditions as the critical water super-saturation or the activation RH. For soot surfaces that were relatively hydrophilic due to ageing, an increase in the reflected light intensity was observed as expected – the reflectivity of the surface increased upon condensation of multi-layers of water on the surface of the black soot. We did not observe such a change for hydrophobic surfaces and the signal remained constant even at high super-saturations (RH > 120%). It is important to note that due to systematic errors, the RH values we report are not necessarily the true RH values inside the cell but the relative changes are indicative of the changes in hygroscopic properties. Our results for relative changes in the RH values at which activation took place provide an insight into the changes occurring on the soot surface during the ageing process. Hence, it is advised to pay more attention to the relative changes in hydrophilic behavior between fresh and aged soot, instead of the absolute activation RH values.

7.2.5 Environmental Scanning Electron Microscopy

A FEI XL30 digital field emission gun Environmental Scanning Electron Microscope (ESEM) was used in this work. This portion of the study was carried out in collaboration with researchers at the Pacific Northwest National Laboratory (Richland, WA). ESEM is a relatively new form of electron-based probe instrumentation, which was originally developed to image non-conductive surfaces. It was only recently that ESEM was successfully adopted to study hygroscopic behavior of individual particles[Ebert et al., 2002]. The ESEM technique is described in detail elsewhere[Donilatos, 1993] but briefly, the ESEM works by dividing the typical SEM high vacuum chamber into several regions of increasing vacuum, separated by pressure-limiting apertures. This setup allows the sample to be maintained at upto 10-20 Torr of residual gas pressure (water vapor in our case) during the imaging process. The sample is placed on a Peltier stage which allows for a temperature control in the range of -10 °C to 60 °C. The entire range of relative humidity (0-100%) can be established for the sample by varying the both the water vapor pressure inside of the chamber and the temperature of the Peltier Stage. This way, hygroscopic behavior and morphological changes during water uptake can be
observed on single particles with a lateral resolution of up to 10 nm. For our experiments, we kept the stage at a constant temperature and varied the water vapor pressure inside the cell at 0.1 Torr increments to observe the hydration of soot particles.

7.3 Results and Discussion

7.3.1 Water uptake on soot surfaces at RH < 100%

QCM was used to measure the water uptake on soot surfaces as a function of relative humidity below saturation (i.e. RH<100%). The change in resonant frequency was directly proportional to the change in mass of soot (due to adsorption of water from the vapor phase) and relative changes in water uptake provided an insight into the changes in the hydrophilicity of the soot. Figure 7-4 shows the change in oscillation frequency as water adsorbed and desorbed from the crystal surface. The reversible adsorption of water vapor was observed as variable mixing of wet and dry flows of He
gas altered the relative humidity inside the sealed QCM chamber. In this particular experiment, soot was substituted by an evenly applied layer of fumed silica (Cabot TS-530) which has the same aggregated physical structure as soot but the surface chemistry is better characterized. When the relative humidity was increased from completely dry conditions (~0% RH), a sharp decline in the frequency signal was noticed, followed by stabilization as equilibrium was reached. The signal returned to the original value once the RH inside the chamber was reduced back down to ~0%. Similar changes were observed for a range of relative humidities and at 101% RH, the surface ‘activated’, signaled by a continuous uptake of water vapor.

Our results for water uptake measurements on fresh and aged soot are summarized in Figure 7-5. The filled and open circles show the relative hydrophobic nature of freshly generated, laboratory soot. Two measurements are shown here to indicate the reproducibility of our measurements. Freshly generated soot was extremely hydrophobic and had a contact angle greater than 135° as observed directly with contact angle measurements (see Figure 7-6a). It is important to note here that we recognize the difficulty associated with defining contact angle for powders and the experimental errors associated with it. We are using the value of contact angle, measured with a drop of water on a powdered surface, as a phenomenological indication of water affinity of the surface. The filled triangles in Figure 7-5 are our results for soot exposed to OH/O3/UV in the presence of water vapor, and they illustrate the increased hydrophilicity of soot at relatively higher RH values. Our contact angle measurements showed that the soot oxidized with OH/O3/UV had a contact angle of approximately 101° (see Figure 7-6b). The open and filled diamonds in Figure 7-5 are our results for soot that was exposed to concentrated HNO3 vapors for 3 hours and 12 hours respectively. As shown in Figure 7-5, reactive uptake of HNO3 acid on soot surface generated hydrophilic ‘active’ centers that adsorbed multilayers of water even under sub-saturation conditions. Figure 7-6c shows the contact angle for soot exposed to HNO3 acid for 3 hours was 90°.

Our results for water uptake on fresh and aged soot show that the chemical changes induced on the soot surface during oxidative uptake are more drastic for exposure to HNO3 than to OH/O3/UV. However, since we cannot estimate the relative concentrations of OH, O3 and HNO3 (g) in these exposures, we cannot inter-compare.
Changes in hydrophilic properties of soot

![Graph showing changes in frequency of water uptake on fresh and aged soot as a function of relative humidity.]

Figure 7-5: Water uptake on fresh and aged soot as a function of relative humidity. Soot treated with HNO$_3$ exhibited the largest increase in hydrophilicity.

Furthermore, our results with the QCM are in general agreement with the contact angle studies. While QCM measures uptake of water at the micro-scale level (less than a few monolayers of water, primarily in the soot micropores), the contact angle studies measure the changes at the macro-scale level (frictional forces between soot surface and a drop of water). Our results indicate that the oxidation of surface functional groups results in changes in the hydrophilic behavior of soot at both micro and macro-scale. Due to these changes, water adsorption from the gas-phase onto soot particles will be enhanced for aged particles, and at the same time, the macro-scale increase in hydrophilic behavior will increase the likelihood of soot entrapment in existing liquid cloud droplets.

Several researchers have reported reversible uptake of water on black carbon and commercial soot at RH < 100% [Disselkamp et al., 2000a; Disselkamp et al., 2000b; Grassian, 2002; Kirchner et al., 2000; Rogaski et al., 1997; Smith and Chughtai, 1996]. In this study, we have, instead, used fresh laboratory generated soot to observe a change in hygroscopic properties of soot upon ageing. Theoretical calculations [Crouzet and...
Marlow, 1995; Wexler and Ge, 1998] show that it is possible for water to condense on soot particles, especially on treated/aged soot with low contact angles (< 90°) and we have shown that while fresh soot has very high contact angles for water, atmospheric ageing can result in reducing the contact angles of soot for water to values similar to ones used in theoretical calculations[ Crouzet and Marlow, 1995; Wexler and Ge, 1998]. Previous studies have also shown that different kinds of diesel, hexane and aged soot exhibit various degrees of water adsorption at low relative humidities[Chughtai et al., 1996; Chughtai et al., 1999a; Chughtai et al., 1999b; Lammel and Novakov, 1995; Weingartner et al., 1997]. We have extended the relative humidity range for water adsorption studies and have shown that even extremely hydrophobic freshly generated soot can become demonstrably hydrophilic upon exposure to oxidizing conditions. Under sub-saturations conditions, water adsorbs reversibly to the soot surface, maintains equilibrium with the surrounding vapor pressure, and can condense as multi-layers on the soot surface even at sub-saturation conditions. Our results are similar to the results obtained by Thomas et al.[Thomas et al., 1999] and Rudich et al.[Rudich et al., 2000] who used a QCM to measure the reversible uptake of water by self-assembled monolayers of organics on gold plated crystals. Adsorption on extremely hydrophobic and relatively hydrophilic species is reversible and the total amount of water adsorbed as a function of relative humidity (under sub-saturation conditions) is strongly influenced by the surface groups exposed (for example, hydrophobic –CH₃ or hydrophilic –OH and –COOH). The presence of hydrophilic organic functional groups on the soot surface, produced during the ageing process, can significantly affect water adsorption, even at low relative humidities. Additionally, Mikhailov et al. [Mikhailov et al., 2001] have shown that hydrophilic soot particles are trapped inside water droplets (and not adsorbed on the surface), resulting in non-reversible entrapment, decrease in particle size and an increase in the fractal dimension due to the densification of the microstructure. Such entrapment of aged soot will result in more efficient removal of soot from the atmosphere.
Figure 7-6: Contact angle measurements for water conducted on: (a) fresh soot, (b) soot exposed to OH/O₃/UV in the presence of water vapor, and (c) soot exposed to concentrated HNO₃ vapor for 12 hours. The contact angle values are 135°, 101°, 90°, respectively.

7.3.2 Water uptake on soot surfaces at RH ≥ 100%

Two different techniques were used to measure the uptake of water on fresh and aged soot surfaces under water supersaturated conditions. Light reflectometry and environmental scanning electron microscopy measured the onset RH at which bulk condensation of water occurred on soot surfaces. In the case of light reflectometry, bulk condensation was observed on a multi-layer thick bed of soot surface deposited on a glass surface, and in the case of ESEM, hydration of single soot particles deposited on thin film TEM substrates was observed.
Figure 7-7: Bulk water uptake on soot aged by exposure to OH/O_3/UV in the presence of water vapor, measured with light reflectometry. The thick solid line indicates the temperature of the soot surface (which controls the RH at a constant water vapor pressure inside the cell) and the thin solid line is the reflected light signal from the soot surface. Upon activation a sharp increase in the signal is observed due to increased reflection from the condensed water layers. See text for details.

Figure 7-7 shows the typical data obtained during the light reflectometry studies. The soot surface was treated with OH/O_3/UV before the experiment was conducted, hence rendering the surface relatively hydrophilic. The thick solid line indicates the varying temperature of the soot surface (which controls the RH) and the thin solid line is the reflected light signal from the soot surface. The intensity of the reflected light from the soot surface is monitored as the temperature of the soot surface is lowered (resulting in an increase in RH). As high relative humidities are reached (RH > 80%), a slight decrease in signal is observed due to changes in the surface soot structure due to multilayer water adsorption. Upon activation at the critical super-saturation, a sharp increase in the reflected light signal is observed due to increased reflection from the condensed water multi-layers. When the RH is lowered again, the signal drops but to a slightly higher
value than the original signal, indicating a restructuring of the soot microstructure. The restructured soot is more condensed and provides a shinier surface to the incident light than the pre-hydration soot surface. Similar results were obtained for soot oxidized by exposure to concentrated HNO₃. In the case of fresh soot, no signal change was observed even at very high super saturations (RH > 115%). In contrast, the data for clean glass surface is presented in Figure 7-8. The reflected light intensity decreases as water multilayers start to build on the glass surface upon activation and when the RH is lowered, the light intensity signal returns to the original value. The contrast between the post-hydration signal levels in Figure 7-7 and Figure 7-8 is another clear evidence of soot surface restructuring and densification upon hydration.
Figure 7-8: Bulk water uptake on clean glass slide measured with light reflectometry. The thick solid line indicates the temperature of the glass surface (which controls the RH at a constant water vapor pressure inside the cell) and the thin solid line is the reflected light signal from the glass surface. Upon activation a sharp decrease in the signal is observed due to decreased reflection from the condensed water layers. See text for details.

Our results from two independent measurement techniques, light reflectometry and ESEM, are summarized in Figure 7-9. Figures 7-9 a, b, c, d, e illustrate the results obtained for the following surfaces using light reflectometry: a=glass slide, b=glass slide treated with an organic silane to make it hydrophobic, c= soot aged with exposure to concentrated HNO₃ vapor for 6 hours, d=soot aged with OH/O₃/UV, e=fresh soot. In our experiments, we have calibrated our system at high relative humidity to the activation of plain glass slide. The measured activation for a plain glass slide was fixed at RH=100.0%. As can be observed, fresh soot did not show hydration even until past RH=115%. This was similar to the results obtained with glass slide coated with a hydrophobic organic silane which also did not show considerable water uptake until past RH=110.5 ± 2%. However, remarkable difference is seen in the hydration RH of aged
soot. Soot that was oxidized with exposure to OH/O₃/UV in the presence of water vapor activated at RH≈102.5 ± 2%. Soot that was exposed to concentrated HNO₃ vapor for 6 hours at room temperature activated at 101.0 ± 2%. These results show that not only does the ageing of soot change the hydrophilicity of soot at lower relative humidities, it also changes the hydration properties, causing soot surfaces to activate at critical supersaturations similar to those observed for extremely hydrophilic surfaces (such as plain glass slide). The dashed vertical lines labeled as (i), (ii), and (iii) indicate the hydration relative humidities observed for fresh and aged soot with the environmental scanning electron microscopy. The ESEM system was calibrated at high relative humidities by measuring the deliquescence of NaCl particles at RH=75%. These lines indicate the following activation relative humidities: (i)= fresh soot, (ii)=soot exposed to OH/O₃/UV in the presence of water vapor, and (iii) soot exposed to concentrated HNO₃. As shown in Figure 7-9, fresh soot does not show activation or hydration until RH=114.9 ± 2%. In contrast, soot aged by exposure to OH/O₃/UV hydrated at RH=106.4 ± 2%, and soot aged by exposure to concentrated HNO₃ hydrated at RH=102.8 ± 2%. The grey-shaded region in Figure 7-9 indicate the super-saturations generally observed in the troposphere.

Even though we cannot compare the exact activation relative humidities (critical supersaturations) between the light reflectometry and the ESEM analysis due to the different degree of oxidation that soot underwent in each case, the drastic differences in the hydration behavior of fresh hydrophobic soot and aged hydrophilic soot are apparent with both experimental techniques. Hydrophobic fresh soot exposed to strong oxidizing environment, by exposure to OH/O₃/UV or to concentrated HNO₃ vapor, becomes hydrophilic enough to activate at critical super-saturations generally found in the troposphere. Our results show that strongly oxidized soot may activate in the troposphere as CCN and compete for available water vapor with other CCN.
Figure 7-9: Bulk water uptake, activation, of fresh and aged soot as observed with light reflectometry and ESEM as a function of RH. (i), (ii), and (iii) indicate the relative humidites at which hydration was observed for fresh n-hexane soot and soot exposed to OH/O₂/UV, and, soot exposed to concentrated HNO₃, respectively. While the exact critical super-saturations required for activation of soot surfaces in light reflectometry and ESEM cannot be compared, the drastic differences changes in hydration of fresh and aged soot are similar in both cases.

Figure 7-10 shows a series of pictures captured during the activation or hydration of a single soot particle. As the relative humidity increases and water condenses on the
soot particle, surface morphology changes due to the collapse within the soot microstructure. Figure 7-10a is a picture of the soot particle before hydration and Figure 7-10f is a picture of the same particle after it has undergone a complete hydration cycle. The changes in soot microstructure, morphology and particle density due to hydration are quite obvious. Soot particle after hydration is more compact, has less porous structure and the collapse of internal microstructures has led to a shrinkage in particle size (average diameter).
7.4 Conclusion

We have conducted an investigation into the changes in hydrophilic properties of fresh laboratory produced soot when it is exposed to oxidizing environments. We have used a quartz crystal microbalance to measure reversible water adsorption on soot surfaces at RH < 100% and have observed that due to ageing, oxidized soot adsorbs more water at lower relative humidities. This increased hydrophilicity can have dramatic impact on the ability of soot particles to be washed out of the atmosphere via entrapment into existing liquid cloud droplets. In addition, presence of several monolayers of water on soot porous surfaces at low relative humidities can affect heterogeneous reaction rates of atmospherically relevant species on soot. Our results with the light reflectometry and environmental scanning calorimetry demonstrate that soot aged by exposure to concentrated HNO$_3$ or OH/O$_3$/UV contains hydrophilic active centers on the surface and undergoes hydration at much lower relative humidities (critical super-saturations) than fresh soot. These results show that aged soot can activate under supersaturated conditions, causing bulk condensation of water on soot surfaces. It has been shown before that only a few active sites are needed for soot to activate (hydrate) and hence, it is possible for soot to compete with other possible CCN in the atmosphere for the available water. Activation of soot as a CCN would greatly affect the residence time of soot in the atmosphere and the cloud albedo.
Chapter 8

FINAL REMARKS

8.1 Conclusions

Laboratory measurements were conducted to understand the microphysics of aqueous atmospheric aerosols. Several different experimental techniques were used, and in some cases developed in-house, to perform the measurements, such as optical microscopy, differential scanning calorimetry, quartz crystal microbalance, light reflectometry, and environmental scanning electron microscopy. Specifically, homogeneous nucleation of ice in NH$_4$NO$_3$-H$_2$O, heterogeneous nucleation by crystallized salt cores in (NH$_4$)$_2$SO$_4$-H$_2$O, heterogeneous nucleation of ice by mineral dust, heterogeneous nucleation of ice by soot, and hydrophilic properties of soot as a function of ageing were studied.

In the case of homogeneous nucleation of ice in NH$_4$NO$_3$-H$_2$O, we have shown that a high degree of super saturation is required before ice crystallizes homogeneously in the aqueous particles. We were not able to reproduce the homogeneous freezing data reported by Cziczo and Abbatt [Cziczo and Abbatt, 2001] and have found the freezing temperatures for NH$_4$NO$_3$-H$_2$O particles to be lower than the previously reported data. We do not think the surface-freezing hypothesis presented in the literature explains the discrepancy between our results and previously published data.
In the case of ice nucleation initiated by crystallized salt cores, we show that the surface defects, micro-structure and morphology play an important role in determining the efficacy of an immersed solid core to nucleate ice via heterogeneous nucleation mechanism. The presence of micro-crystallites of solid ammonium sulfate act as potent ice nuclei in equilibrium with binary NH₄HSO₄-H₂O particles and may play an important role if they can exist in the atmosphere in equilibrium with aqueous mixed salt aerosols. Close to the boundaries between clouds and clear air, for example, aerosol particles and cloud droplets can undergo several thermal cycles, resulting in large temperature fluctuations and repeated freezing and melting events with the particles. This thermal history of the particles may be important in determining the nucleation mode for the formation of stable ice clouds.

In the case of mineral dust, our results show that kaolinite and montmorillonite can act as efficient ice nuclei in (NH₄)₂SO₄-H₂O particles. Since the two dusts studied as ice nuclei had remarkably different surface chemical groups exposed to the aqueous solutions, and yet they showed similar ice-nucleating efficacy, we think the morphology and microstructure of the immersed solids may play a more important role in heterogeneous ice nucleation. Even though our data is in better agreement with available field data than the homogeneous freezing results, it still deviates significantly at low temperatures. Further work is required to understand quantitatively the effects of increased surface area and surface defects that may provide 'active' sites for ice nucleation to occur.

We did not find soot, fresh or aged by exposure to OH/O₃/UV in the presence of water vapor or to concentrated HNO₃, to be a good nuclei for ice in (NH₄)₂SO₄-H₂O particles. Even though EDX analysis of the changes in surface chemistry due to oxidation indicate a reactive uptake of gas-phase species in the oxidizing environments, the similar ice-nucleation activity of fresh and oxidized soot indicate that the ice-nucleation potential of soot may also be primarily determined by soot morphology rather than by surface chemistry. This conclusion is further confirmed by other studies that have shown water to remain in liquid form in the micropores of kerosene soot even at very low temperatures.

Since soot is found ubiquitously in urban, rural and remote atmospheres, we have conducted an investigation of the changes in hydrophilic properties of soot before and
after exposure to ageing environments. We used a quartz crystal microbalance to measure reversible water adsorption on soot surfaces at RH < 100% and have observed that due to ageing, oxidized soot adsorbs more water at lower relative humidities. This increased hydrophilicity can have dramatic impact on the ability of soot particles to be washed out of the atmosphere via entrainment into existing liquid cloud droplets. In addition, presence of several monolayers of water on soot porous surfaces at low relative humidities can affect heterogeneous reaction rates of atmospherically relevant species on soot. Our results with the light reflectometry and environmental scanning calorimetry demonstrate that soot aged by exposure to concentrated HNO₃ or OH/O₃/UV contains hydrophilic active centers on the surface and undergoes hydration at much lower relative humidities (critical supersaturations) than fresh soot. These results show that aged soot can activate under supersaturated conditions, causing bulk condensation of water on soot surfaces. It has been shown before that only a few active sites are needed for soot to activate (hydrate) and hence, it is possible for soot to compete with other possible CCN in the atmosphere for the available water. Activation of soot as a CCN would greatly affect the residence time of soot in the atmosphere and the cloud albedo. The change in the hydrophilic properties of soot may increase the average cloud albedo by shifting the size of cloud particles to smaller values, lead to suppression of rain, cause local heating of the cloud layer due to absorption of radiation by soot and affect the rate and nature of heterogeneous reactions on soot surface.

8.2 Ideas for future research

Laboratory measurements and field experiments have shown that both homogeneous and heterogeneous nucleation are important mechanisms for the formation of ice clouds in the troposphere. Our results included in this thesis indicate that surface morphology, microstructure and chemical constituents determine the ice-nucleating efficiency of ice nuclei in the immersion mode. At present it is extremely hard to identify 'active' sites for ice nucleation on immersion nuclei and future experiments will need to better characterize the surface chemistry and morphology of the mineral, inorganic and
organic material that can trigger heterogeneous nucleation of ice in aqueous atmospheric particles.

Soot is an extremely complicated material, both chemically and morphologically. The microstructure of soot and its aggregate, fractal, porous nature lends to complex thermodynamic properties, while the surface chemical groups change rapidly as soot ages in the atmosphere. Our results show that aging of soot in the atmosphere can drastically change its hydrophilic properties. While fresh soot is extremely hydrophobic, and not very active in aqueous processes, soot oxidized by OH/O3/UV in the presence of water vapor and by exposure to concentrated HNO3 vapors develops hydrophilic centers which lead to the hydration of soot at relatively lower relative humidities. The increased ability of aged soot to attract and retain water molecules drastically changes the probably for the entrapment of soot in existing liquid particles, and if sufficiently hydrophilic centers are created on the soot surface during oxidation, soot may also compete as a CCN in polluted atmospheres. To further understand the mechanisms of aging of soot such as exposure to reactive trace gas species of interaction with soluble inorganic aerosols, as well as to quantify the change in hydrophilic behavior of soot as a function of exposure time in controlled aging environments, careful experiments should be conducted. Such experiments would greatly reduce the uncertainty in the lifetime of soot in the atmosphere, and also help understand the role of soot in atmospheric processes.
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Research
1998-present Physical/Environmental Chemistry, Prof. Mario J. Molina
Laboratory research on physical and chemical processes that affect global warming, air pollution and health. Experience with nano-particles, laser-techniques and sophisticated analytical instruments. Led and managed a team of 4 people in research on the chemical fate of hydrocarbon soot in oxidizing environments. Authored publications in major research journals and work was reviewed in 'Nature'.
CAMBRIDGE, MA

1997-1998 Biophysical Chemistry, Prof. Virginina B. Pett and Charles M. Borders
Developed a method for systematic search of structurally important arginine and lysine amino acids in Brookhaven National Laboratory's Protein Database. Undergraduate thesis.
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Reconstructed, upgraded and managed analytical chemistry research instruments.
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Leadership/Entrepreneurship
2001-present Business Development
Business Information and Management Services
Developed business and marketing strategies for a startup in Pakistan to penetrate the USA market for medical data service provider. Performed market research on competitors, technologies, services, pricing and co-authored business plan for launching US subsidiary. Developed relationships with strategic partners. Currently developing a business plan for an international nurse placement program in collaboration with nursing colleges in Asia, Europe and Africa.
USA & PAKISTAN

2001-present Strategy Consultant
Junoon, Inc.
Developed marketing strategy for a major fusion rock band from Pakistan to launch their first album in USA (EMI Records). Initiated and maintained strategic relationships for the band and organized US concert tour.
USA & PAKISTAN

1998-present Career Development Chair
Harvard/MIT European Club
Organized and managed three Harvard/MIT annual European career fairs, founded the first pan-European Startup Summit and the first Euro-US Biotech Summit at MIT. Led large teams in the organization of successful corporate recruiting/networking events, and implemented marketing and business strategies in club's operations that increased the annual revenue by 300 percent over a 3-year period.
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2000-present Consultant
International Federation of Medical Students' Associations
Consulted to the executive board of an international federation of 76 national medical student organizations worldwide. Organized and led fundraising campaigns (for more than $1 million), co-authored strategy papers on fundraising and project management. Advisor to international workshops on 'Poverty and Health' (Denmark), 'HIV and Human Rights' (Indonesia & South Africa), 'Refugee Health' (Pakistan).
CEDEX, FRANCE

2000-2002 Founding President
Foundation Action for Healthier Future
Authored organizational by-laws, developed governing structures and worked with international Board of Directors to institute strategies for fundraising, networking, local organization management, public relations and international advocacy for an international non-profit operating in the fields of human development, public health and empowerment of youth.
USA & THE NETHERLANDS
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**Founding Director**
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Founded an international policy think-tank on social, political, economic and cultural issues facing developing countries. Worked with the Ministry of Education and Ministry of Science and Technology to draft recommendations for reforms in higher education for Pakistan. Presided over an international conference on recommendations that were approved by the Government of Pakistan.

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**Co-producer and Director**
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Co-produced and directed an official documentary on muslim students at MIT. Co-authored script, conducted video interviews, led group discussions and assisted in post-production.

**Activities**

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- **William H. Galpin Prize** - The College of Wooster
- **Robert E. Wilson Prize in Chemistry** - The College of Wooster
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