NUMERICAL SIMULATIONS ON THE
REDISTRIBUTION OF ATMOSPHERIC TRACE CHEMICALS
THROUGH CLOUD PROCESSES

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Jen-Ping Chen

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We approve the thesis of Jen-Ping Chen.

Dennis Lamb  
Associate Professor of Meteorology  
Thesis Advisor  
Chair of Committee  
Date of Signature  
8 October 1992

William H. Brune  
Associate Professor of Meteorology  
Date of Signature  
8 October 1992

James F. Kasting  
Associate Professor of Geosciences  
Date of Signature  
8 Oct 1992

Robert J. Heinsohn  
Professor of Mechanical Engineering  
Date of Signature  
Oct 8, 1992

Akhlesh Lakhtakia  
Associate Professor of Engineering  
Science and Mechanics  
Date of Signature  
12 Oct 1992

Dennis W. Thomson  
Professor of Meteorology  
Head of the Department of Meteorology  
Date of Signature
ABSTRACT

The redistribution of atmospheric trace substances through cloud processes is investigated using a detailed microphysical and chemical cloud model. A multi-component categorization scheme is used in the model to group cloud particles into different bins according to their various properties. Cloud drops are categorized in both their water mass and solute mass components. This liquid-phase particle framework is useful in calculating warm-cloud processes such as the concentration-dependent chemical transformations, and the activation and condensation growth processes that are sensitive to the CCN distribution. The behavior of ice-phase particles is even more complicated than the droplets due to the wide range of possible growth rates, shapes and surface areas, factors which then also influence other microphysical, chemical, and radiative processes. An extra "shape" component is thus included in the ice-phase particle framework to describe the distribution of ice-phase particles. Special efforts are paid to develop the theory and parameterization for the change of the growth habits for ice particles.

In dealing with a model that inevitably has a large dimension, a hybrid bin-method is applied so that it can maintain the conservation of all properties and, at the same time, perform fast and accurate calculations for transferring various properties between categories in the multi-component systems. With a minimum of parameterization, this model is capable of simulating detailed microphysical and chemical processes that occurred during cloud and precipitation formations.

In the earlier stage of the study, it is shown that the drop number concentration is a function of both the water mass and the solute mass in the drops, a phenomenon that cannot be resolved by conventional cloud models. Applying the detailed microphysics in
a parcel model, it is also shown that the number concentration of ice particles is indirectly controlled by the number concentration of cloud condensation nuclei. Bulkwater models that can not treat the in-cloud supersaturation are not able to properly simulate such processes.

The concept of the relative removal efficiency (a measure of the ability of a chemical species to be removed in the precipitation compared to that of water) was introduced and tested in a simple particle model in the earlier stage of the study. An extended test on the relative removal efficiencies was done by simulating a wintertime, orographic cloud with the complete model. Satisfactory results for both the microphysical and chemical behavior of the cloud are produced in the simulation. It is shown that the redistribution of atmospheric trace substances is controlled by their microphysical pathways.
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Chapter 1

INTRODUCTION

Atmospheric trace constituents play significant roles in the global budgets of water, chemicals, and radiation and eventually lead to the control of climate. Susceptible to anthropogenic influences, these trace constituents comprise a vulnerable link in the maintenance of the earth system. Thus, cloud processes, which play a very important role in regulating the distribution of the atmospheric trace constituents, need to be carefully studied in order to understand the tolerance of nature to human activities.

Cloud is the dominant place, besides the Earth's surface, where atmospheric constituents can exist in the aqueous phase. The uptake of trace chemicals by atmospheric particles typically occurs in the cloud. These constituents become partially or wholly dissolved in the cloud water, sorbed by cloud ice, or fixed in a nonvolatile form by means of chemical transformations that are not significant elsewhere in the atmosphere. Constituents that are particularly soluble or nonvolatile can be removed effectively from the atmosphere by precipitation processes and deposited on the terrestrial surface. Therefore, we can regard the cloud as a potentially efficient machine for the removal of atmospheric trace chemicals. So, cloud processes have the general effect of offsetting the air pollution problem, although at the expense of creating acid rain and related problems. The remainder of the trace chemicals, either in their gaseous or particulate forms, then enter the global atmospheric background where they may affect the global radiation budget. The trace chemicals, either those deposited onto the earth's surface or those remaining in the air, can also interact with biospheric activities. Such interactions may cause nonlinear feedback effects on the climate. Also, the particulate trace constituents in the atmosphere, modified in both the composition and number
concentration, can again serve as cloud forming nuclei for later cloud development and thus alter the precipitation patterns in nonlinear ways. All these effects, either short term or long term, are interrelated through the cloud processes. Any disturbance to one component affects the others. Especially today, as anthropogenic sources of the atmospheric chemicals become stronger without a commensurate strengthening of the sinks, a greater burden is put into the atmosphere and so a greater reliance must be placed on the wet removal processes. Therefore, it is all the more important to understand the physical and chemical processes in the cloud.

However, the cloud processes are complex and mutually interactive, involving many scientific disciplines and nearly all aspects of meteorology. The scale of the problems of concern extends over a broad range -- from molecular scale to global scale. Research on various aspects of the problems has been done, with progressive understanding of the cloud processes. Observations are often used to study the physics and chemistry of the cloud processes, but the variability of the natural situation is large and associated with uncertain boundary conditions. Also, while the ongoing field-study programs continue to expand the environmental data base, more investigation is needed to provide insight into the fundamental physical and chemical mechanisms that control the cloud processes. Theoretical approaches or laboratory experiments are alternative ways of studying the processes in a controllable way. Due to the potential for nonlinearity, however, the interactions between different mechanisms are often difficult to handle. The use of models to assemble the theoretical concepts and numerical techniques to approximate the real world is, therefore, an important way of investigating the cloud processes and their interactions with the earth system.

Numerical modeling is currently an active means for studying the physics and chemistry of clouds. Due to limitations of computer resources and imperfect knowledge of the subject, each numerical modeling effort must focus on some aspect of the problem
and use simplifications and parameterizations to some degree. For instance, Tripoli and Cotton (1982), as well as Farley and Orville (1986), used bulk-water parameterizations for the microphysics in order to gain more details about the dynamics in two or three dimensions; Hall (1980) used a two-dimensional slab-symmetric dynamic framework to incorporate detailed treatment of the water and ice particles but did not consider cloud chemistry; Flossmann and Pruppacher (1988) extended Hall's work with the addition of aerosol scavenging and equilibrium chemistry for sulfur species, but neglected the cold-cloud (ice phase) processes; Tremblay and Leighton (1986), as well as Niewiadomski (1989), used a three-dimensional model with parameterized (no explicit physics) warm-rain development and kinetic oxidation of sulfur dioxide to simulate the convective and turbulent transport of sulfur species; Pandis and Seinfeld (1989), as well as Topalian and Montague (1989), used a very detailed kinetic reaction scheme of the aqueous-phase chemistry for the scavenging of pollutant gases, but included no microphysics or dynamics; Giorgi and Chameides (1986) used a first-order parameterization to simulate rainout in a photochemical model within a general circulation model without explicit cloud physics. The evolution of cloud chemistry research has demonstrated the necessity of using more detailed physics and chemistry. However, with only finite computational resources available in the foreseeable future, parameterizations and simplifications are to some extent inevitably needed.

One purpose of the current study has therefore been to develop a numerical scheme for simulating the cloud processes, with particular emphasis on the detailed microphysics and chemistry. Although most other processes have been fairly well studied, it is felt that the ice phase physics and chemistry are still poorly understood and yet very important. Another of the intended goals of this study is to fill in some of the traditionally missing links with recent experimental data and to update the current modeling studies. The numerical model, when sufficiently detailed, can serve as an
effective tool for testing the atmospheric importance of the particular processes studied in the laboratory. Beyond the initial stage of focusing on some specific mechanisms of microphysics or chemistry, a study relating the individual processes to a fully interactive system is crucially needed. A preliminary study (Lamb and Chen, 1988) was performed to show that microphysical processes in clouds can have significant influence on the fractionation and the removal efficiency of chemicals in clouds. A similar conclusion was also reached by Hegg and Hobbs (1988). An extension of the earlier modeling study (Lamb and Chen, 1990) further demonstrated that the ice phase microphysics plays an important role in the scavenging of trace chemicals by clouds. Using laboratory results from Lamb and Blumenstein (1987) and Iribarne and Pyshnov (1988), it was shown that there is a significant difference in the removal efficiencies with different chemical parameterizations and the types of microphysical processes involved. Therefore, a detailed model with adequate microphysics and chemistry in both liquid and ice phases, as intended in this study, is certainly a necessity.

Clouds have frequently been studied with so-called bulk-water models, which use prescribed size distributions for the cloud particles and keep track only of the bulk properties of the whole population. However, individual cloud drops act differently from bulk water in nonlinear ways. Bulk-water parameterizations may therefore give misleading results in cloud chemistry (Hegg, 1989; Hegg and Larson, 1990). In contrast, detailed cloud models allow the cloud-particle size spectra to evolve naturally according to explicit physics (e.g., Flossmann et al., 1985; Tzivion et al., 1987). However, most conventional detailed cloud models resolve the particle spectra according to the particle size or mass only. In such models, all particles of the same size necessarily have exactly the same physical and chemical properties. Nevertheless, drops of the same size do not necessarily contain the same amount of solute (Chen and Lamb, 1992a). Since chemical equilibria and reaction rates in the cloud water are controlled by the chemical
composition and pH values (Millero et al., 1989; Jayne et al., 1990), conventional
detailed cloud models can not resolve the non-linear chemical processes that frequently
occur in clouds. Therefore, the liquid-phase particle spectrum is categorized with an
additional solute component in this study. Some preliminary results using such a
multi-component particle framework have been presented by Chen and Lamb (1992a).
Note that the only other model known to use a multi-component categorization scheme
up to this date is the work by Roelofs (1992), but that model does not include any
ice-phase processes. The categorization of the ice particles is especially complicated
because ice particles that have the same mass do not necessarily have the same size or
shape. Conventional detailed cloud models are not able to resolve the complicated shape
of ice particles and their growth habits, which are important factors that control both the
ice-phase microphysics and at least some of the cloud chemistry. A third categorization
component (shape) is therefore necessary for a proper simulation of the evolution of ice
particles, so it is included in this study.

The development of the present model also stresses the flexibility of its
application to various domains of interest. It is a module that can be incorporated into a
dynamic framework or used simply with prescribed wind fields. Alternatively, it could
be implemented in either a multi-dimensional model or a simple box model. A model
that deals with fewer than three dimensions or a limited number of processes necessarily
sacrifices some aspect of reality, but quite often such a model can lead to valuable insight
about the microphysical behavior of clouds that would not otherwise be obtained within
the constraints of human perception or computational resources.

The present model has been developed with emphasis not only for studying the
physical and chemical mechanisms and their interactions, but also for applications such
as testing laboratory results. Because of the large amount of details included, this model
is computationally very intensive. It is not feasible to incorporate the model directly into
multi-dimensional dynamical models, at least at this stage. However, it can be used to generate bulk-water parameterizations using statistical methods. Such parameterizations, when fully developed, would be based on fundamental physical principles instead of ad hoc relationships and prescribed size distributions, and yet permit efficient calculations for the microphysical processes (Lee, 1989, 1990). This model can also be used for developing higher-level parameterizations for the redistribution of atmospheric chemicals by clouds, which can be applied in large-scale dynamical models or climate models.

The main goals of this study are to develop the detailed microphysical and chemical model and then apply it in a study of the redistribution of atmospheric trace substances through cloud processes. The next chapter gives the necessary theoretical discussions of the physics and chemistry that are included in this study. We first discuss the thermodynamics that is fundamental to the cloud microphysical and chemical processes in Section 2.1. The theories for the liquid- and ice-phase microphysics are given in Section 2.2 and 2.3, respectively. Then, the liquid- and ice-phase chemistry are given in Section 2.4 and 2.5, respectively, followed by a general summary in Section 2.6. Chapter 3 gives the numerical techniques developed and applied in this study. Section 3.1 describes the multi-component particle framework and the bin methods, which form the foundation of the computation schemes. Section 3.2, 3.3, and 3.4 give some of the nonconventional methods that have been used in solving various microphysical processes. Section 3.5 treats the methods for the liquid-phase chemistry and Section 3.6 lists miscellaneous numerical methods that help the computational efficiency, followed by a short summary. Chapter 4 gives the results of the numerical simulations. Section 4.1 to 4.3 are preliminary results that were published earlier. Section 4.4 contains the results of a full-scale simulation of a two-dimensional steady-state orographic cloud. Chapter 5 gives the general summary and future work plans.
The formation of clouds involves various microphysical and chemical processes. In order to study clouds in detail we need to know the theories behind these processes. The first part of this chapter introduces the fundamental thermodynamics, which provides the basis for the growth theory of cloud particles. The discussion of thermodynamics is followed by two sections that describe the microphysical processes for the growth of liquid- and ice-phase particles. The following two sections are then devoted to a discussion of the liquid- and ice-phase chemical processes that are included in this study.

2.1. Fundamentals of Thermodynamics

Thermodynamics is fundamental to microphysical processes that involve phase changes. This section introduces various thermodynamic equations that are derived from the concepts of free energy and chemical potential.

1. Gibb's Free Energy and Chemical Potential

The Gibb's function (also called the Gibbs free energy) of a system is defined as (Zemansky and Dittman, 1981, p. 219):

\[ G \equiv H - TS \equiv U + PV - TS \]

(2.1)
where $H, T, S, U, P, V$ are the enthalpy, temperature, entropy, internal energy, pressure and volume of the system, respectively. The effect of the change in the amount of a component $k$ in the system on the Gibbs function is expressed by the chemical potential

$$
\mu_k = \frac{\partial G}{\partial n_k},
$$

(2.2)

where $n_k$ is the number of moles of the $k$th component. The exchange of heat, mass and work of a system with its environment can be expressed by the change of the chemical potential (Dufour and Defay, 1963)

$$
d\mu_k = \alpha_k dP_k - s_k dT + RT d\ln a_k, \quad (2.3)
$$

where $\alpha_k, P_k, s_k, a_k$ are the molar specific volume, partial pressure, molar specific entropy, temperature, and the activity of component $k$, respectively, and $R$ is the universal gas constant. Each component can be in the gas-, liquid-, and solid-phases.

2. Water System

Let us consider the major component in cloud particles -- water. By dropping the subscript $k$ and replacing it with $v, w, i$ to represent the vapor-, liquid, and ice-phases of water, respectively, we can express the change of chemical potentials as

$$
d\mu_v = \alpha_v dP_v - s_v dT + RT d\ln a_v, \quad (2.4)
$$

$$
d\mu_w = \alpha_w dP_w - s_w dT + RT d\ln a_w, \quad (2.5)
$$

$$
d\mu_i = \alpha_i dP_i - s_i dT + RT d\ln a_i. \quad (2.6)
$$

The total pressure in the gas-phase is the sum of the pressure of dry air ($P_{air}$) and the partial pressure of water vapor ($e$)

$$
P_v = P_{air} + e. \quad (2.7)
$$
With phase changes of water, the pressure of dry air is constant and the change of total pressure \( dP_v \) is simply the change of vapor pressure \( de \). The pressure in the liquid is the sum of the pressure from the gas-phase exerted on the liquid and the pressure from the molecular attraction in the liquid. Neglecting the pressure from gravitational acceleration (i.e., the weight of water), we note that pressure may exist due to the surface tension of the liquid drop. The condition of mechanical equilibrium inside a drop is given by the *Laplace formula* (Pruppacher and Klett, 1980, p. 102):

\[
P_w = P_v + \frac{2 \sigma_{w/a}}{r},
\]

(2.8)

where \( \sigma_{w/a} \) is the surface tension between water and air, and \( r \) is the radius of the drop. If we assume ideal gas behavior, the activity of water in the gas-phase is written as

\[
a_v = x_v = \frac{e}{P_v},
\]

(2.9)

where \( x_v \) is the mole fraction of water vapor and \( e \) is the vapor pressure in the air. The activity of water in ideal solution is

\[
a_w = x_w = \frac{n_w}{n_w + i_s n_s},
\]

(2.10)

where \( x_w \) is the mole fraction of water in the liquid, \( n_w \) and \( n_s \) are the number of moles of water and solute in the drop, and \( i_s \) is the dissociation coefficient of the solute. For the phase-transition equilibrium between water vapor and liquid water, \( d\mu_v = d\mu_w \), we can combine (2.4) and (2.5) to find

\[
0 = \alpha_v de - \alpha_w dP_w - (s_v - s_w) dT + \mathcal{R} T d\ln \frac{a_v}{a_w},
\]

(2.11)

Note that \( (s_v - s_w) \) is the change of specific entropy during phase change between the vapor- and liquid-phases, and equals the molar latent heat of evaporation \( l_e \) divided by the
temperature. Replace the pressure inside the liquid $P_w$ with the condition of mechanical equilibrium to get

$$0 = (\alpha_v - \alpha_w) d\epsilon - \alpha_w \frac{2\sigma_{w/a}}{r} d\epsilon - \frac{l_e}{T} dT + \frac{R T d\ln a_v}{a_w}. \quad (2.12)$$

This equation is used to derive the relationship between various parameters under equilibrium conditions, as described below.

3. **Clausius-Clapeyron Equation**

First, let us investigate the saturation vapor pressure over a solution drop, $e_s(r, a_w, T)$, as a function of drop radius $r$, the activity of water $a_w$, and temperature. By setting the conditions for the saturation vapor pressure ($a_v = \text{constant}$) over pure water ($a_w = 1$) with flat surface ($r = \infty$), we have the following relationship:

$$(\alpha_v - \alpha_w) d\epsilon = \frac{l_e}{T} dT. \quad (2.13)$$

Since $\alpha_v \gg \alpha_w$ and $P_{\text{air}}$ is constant during phase change, we have

$$d\epsilon \approx \frac{l_e}{\alpha_v T} dT = \frac{e l_e}{RT^2} dT, \quad (2.14)$$

which is the **Clausius-Clapeyron equation**. As a first approximation, particularly for small variations of $T$, $l_e$ may be considered to be constant. Then, we may write the Clausius-Clapeyron equation in an integrated form as

$$\frac{e_s(x,1,T)}{e_s(x,1,T')} = \exp\left(\frac{l_e}{R} \frac{(T - T')}{TT'}\right), \quad (2.15)$$

where $T'$ is a reference temperature.
4. Kelvin's Equation

The variation of water vapor pressure over a pure water drop \((a_w = 1)\) of radius \(a\) can be shown by fixing the temperature \((dT = 0)\) and the total gas pressure \((dP_v = 0)\) in (2.12):

\[
0 = -a_w \frac{2 \sigma_{w/a}}{a} + R_T d \ln a_v . \tag{2.16}
\]

Integrate this equation between \(\infty\) and “\(a\)” and one has

\[
a_w \frac{2 \sigma_{w/a}}{a} = R_T \ln \frac{e_s(a,1,T)}{e_s(\infty,1,T)} , \tag{2.17}
\]

where \(e_s(a,1,T)\) is the saturation vapor pressure at the drop surface and \(e_s(\infty,1,T)\) is saturation the vapor pressure over a flat water surface. This leads to the Kelvin equation

\[
\frac{e_s(a,1,T)}{e_s(\infty,1,T)} = \exp\left(\frac{2 \sigma_{w/a}}{R T a}\right) = \exp\left(\frac{2 \sigma_{w/a}}{\rho_w R_v T a}\right) , \tag{2.18}
\]

where \(R_v\) is the gas constant of water vapor and \(\rho_w\) is the density of liquid water.

5. Raoult's Effect

The effect of solute on the vapor pressure can be shown by examining a flat water surface with fixed \(T\) and \(P_v\) in (2.12), so that

\[
0 = R_T d \ln \frac{a_v}{a_w} \tag{2.19}
\]

which is simply the Raoult’s law

\[
a_v = \frac{e_s(0,a_w,T)}{e_s(0,1,T)} = a_w = x_w . \tag{2.20}
\]
6. Köhler Equation

Considering the same situation as in the previous case but include the curvature effect of a droplet, one has

\[ \alpha_w \, d \left( \frac{2 \sigma_{wa}}{r} \right) = \mathcal{R} \, T \ln a_e \frac{a_e}{a_w} \]  

(2.21)

Integrate it from \( r = a \) to \( \infty \), and \( a_w = a_w \) to 1 to obtain the Köhler equation:

\[ \frac{e_s(a, a_w, T)}{e_s(\infty, 1, T)} = a_w \exp \left( \frac{2 \omega_{wa}}{a \rho_w R \gamma} \right). \]  

(2.22)

7. Freezing Point Depression

Equations (2.3) to (2.22) describe the basic thermodynamic equilibria in the vapor-liquid system. A similar approach can be used to find the relationship between vapor-ice and liquid-ice. An example of the liquid-ice equilibrium is the effect of solute on the freezing point of water. Considering only the entropy and the activity terms for the equilibrium between water and ice, one has

\[ \mathcal{R} T \, d \ln \frac{a_w}{a_i} = (s_w - s_i) \, dT = \frac{l_f}{T} \, dT, \]  

(2.23)

where \( a_i \) is the activity of ice (\( \approx 1 \)) and \( l_f \) is the molar latent heat of fusion. Rearrange the last equation so that

\[ \frac{1}{T^2} \, dT = \frac{\mathcal{R}}{l_f} \, d \ln a_w. \]  

(2.24)

Integrating from \( T_o \) (the freezing point of pure water where \( a_w = 1 \)) to \( T \) (the freezing point corresponding to the activity of water \( a_w \)) and assuming \( l_f \) is constant in the temperature range of interest, the expression becomes
\[-\left(\frac{1}{T} - \frac{1}{T_o}\right) = \frac{R}{l_f} \ln a_s = \frac{R}{l_f} \ln(1 - a_s) \]  \hspace{1cm} (2.25)

where \(a_s\) is the activity of solute. For low solute concentrations, \(\ln(1 - a_s) \approx -a_s\), and \(T T_o \approx T_o^2\), so we can write the result for ideal solution as

\[
\delta T = T_o - T = \frac{RT_o^2}{l_f} a_s = \frac{RT_o^2}{l_f} x_s ,
\]  \hspace{1cm} (2.26)

where \(x_s\) is the mole fraction of solute, and \(\delta T\) is the \textit{freezing point depression}.

\textbf{8. Solubility}

The solubility of a solute in certain solutions may be estimated by the equation for chemical potential (2.3). Since the undissolved solid solute is in chemical equilibrium with the dissolved solute in a saturated solution, we may write the equilibrium relationship as

\[
\mathcal{R} T d \ln \frac{x_l}{x_s} = (s_l - s_s) dT = \frac{\Delta h}{T} dT ,
\]  \hspace{1cm} (2.27)

where \(s_l\) and \(s_s\) are the specific entropies in the liquid- and solid-phases, \(x_l\) and \(x_s\) (\(= 1\)) are the mole fraction of the solute in the saturated solution and the solute in the solid, and \(\Delta h\) is the specific heat of dissolution. Similar to the Clausius-Clapeyron equation, the last equation rearranges to

\[
d \ln x_l = \frac{\Delta h}{\mathcal{R} T^2} dT .
\]  \hspace{1cm} (2.28)

If we assume that \(\Delta h\) is constant over the temperature range of interest, we obtain the integrated form

\[
x_l(T) = x_l(T') \exp \left( \frac{\Delta h}{\mathcal{R}} \frac{(T - T')}{TT'} \right) ,
\]  \hspace{1cm} (2.29)
where $T'$ is a reference temperature. The solubility $Q_s$ of a solute substance can be defined as the mole fraction of solute in the saturated solution:

$$Q(T) \equiv x_s(T) = Q_s(T')\exp \left( \frac{\Delta h (T - T')}{RT'} \right), \quad (2.30)$$

where $Q_s(T')$ is the solubility at the reference temperature $T'$. For most nonvolatile substances, $\Delta h$ is greater than zero and, therefore, the solubility increases with increasing temperature.

9. Phase-Diagram of a Solution

The discussion in this section is focused on the determination of the deliquescence of haze particles as well as the freezing of both dilute and concentrated drops. The freezing-point equilibrium and the solubility equilibrium discussed previously play analogous roles in thermodynamics. The combination of the two equilibria composes the phase diagram for a solution. Figure 2.1 gives an example of the phase diagram for a water solution containing ammonium sulfate. Each of the constituents in the solution has an equilibrium point between its liquid- and solid-phases that is uniquely defined by its mole fraction and the temperature. At temperatures and solute concentrations below Curve A, water tends to precipitate out as ice. Similarly, ammonium sulfate will precipitate out as solid at lower temperatures and higher concentrations than that indicated by the curve B. At a point below both curves, both constituents may precipitate out and form solid mixtures. The interception of the two equilibrium curves is called the eutectic point. It is well known that water does not necessarily freeze when the temperature is below the freezing point but may remain in a supercooled liquid state. The dashed curve A' indicates the maximum possible supercooling, which is about 40°C (Rasmussen and Luyet, 1970). Below this curve,
water will freeze spontaneously. A situation similar to the supercooling of water is the 
*supersaturation* of solute in the solution. There is no detailed information about the 
maximum supersaturation of ammonia-sulfate in water. However, Shaw and Rood 
(1990) measured the humidities at which the solute in haze particles crystallizes 
spontaneously. They showed that the *crystallization humidity* at 60°C is about 40% for 
ammonia-sulfate solutions. The solute concentration in haze particles under low relative 
 humidities can be proven to be quite constant with respect to the particle size. The 
solute concentration for the above condition is about 36 M, which translates to a mole 
fraction of about 0.39 as shown by the point $X$ in Figure 2.1. The curve $B'$ is an 
etrapolation of the spontaneous crystallization point, drawn to be parallel to curve $B$. 
From the diagram, we can estimate that the spontaneous crystallization occurs at a solute 
concentration of about $Q_s(T) + 0.29$.

![Figure 2.1: Phase diagram for ammonia-sulfate solution. Curve A and B are the 
equilibrium curves for water and ammonia-sulfate while A' and B' are the 
spontaneous nucleation curves. The horizontal axis is the mole fraction of 
ammonia-sulfate in the solution.](image)
10. Definition of the Total Heat

Traditional cloud models assume that the sensible heat contained in cloud particles is negligibly small so that the heat equation can be simplified and only the latent heating need to be considered (e.g. Wisner et al., 1972; Miller and Young, 1979; Hall and Pruppacher, 1976). By defining the "total heat" here, we can not only keep track of the energies contained in different types of cloud particles but also simplify the heat transfer calculation for cloud processes. The molar specific enthalpy for a system that involves only work of expansion is defined as follow:

\[ h = u + P\alpha - sT + \text{constant} = \int c_p dT - sT + b, \]  

(2.31)

where \( u \) is the molar specific internal energy, \( c_p \) the molar heat capacity at constant pressure, and \( b \) is a constant that represents a reference energy level. For water vapor, liquid water, and ice, we have

\[ h_v = \int c_{p_v} dT - s_v T + b, \]
\[ h_w = \int c_{w} dT - s_w T + b, \]  

(2.32)
\[ h_i = \int c_{i} dT - s_i T + b, \]

where \( c_{p_v} \), \( c_{w} \), and \( c_{i} \) are the molar specific heat capacities of water vapor, liquid water, and ice, respectively. The first terms on the right hand sides of each equation represent the sensible heats of water molecules in the different phases. However, the evaluation of these integrals, starting from its lowest state (\( T = 0 \) K), is generally not available. It is also very cumbersome to carry around the constant \( b \). Since our major concern will be the "differences" between these total heats, and the change of the specific heat capacities in the temperature range of interest is small, we can define a specific total heat \( h \) by choosing a particular reference energy level. With \( l_v = (s_i - s_v) T \), and \( l_f = (s_i - s_w) T \), the above equations can be rewritten as
\[ h_v = \int_0^{T_v} c_{p_v} \, dT + \int_{T_v}^{T_w} c_{r_v} \, dT + l_v(T_v) + b', \]
\[ h_w = \int_0^{T_w} c_{w} \, dT + \int_{T_w}^{T_i} c_{w} \, dT + l_f(T_w) + b', \]
\[ h_i = \int_0^{T_i} c_i \, dT + \int_{T_i}^{T_o} c_i \, dT + b', \]

(2.33)

where \( T_v, T_w, \) and \( T_i \) are the temperature of water vapor, liquid water and ice, respectively, and \( b' = b - s_i T. \) Since the difference between the enthalpy of water of different phases at the triple point \( T_o \) is simply the latent heat, we have

\[ h_v(T_o) = \int_0^{T_v} c_{p_v} \, dT + l_v(T_v) + b' = h_i(T_o) + l_v(T_v), \]
\[ h_w(T_o) = \int_0^{T_w} c_w \, dT + l_f(T_w) + b' = h_i(T_o) + l_f(T_w), \]
\[ h_i(T_o) = \int_0^{T_i} c_i \, dT + b', \]

(2.32)

where

\[ \int_0^{T_v} c_{p_v} \, dT + b' = \int_0^{T_w} c_w \, dT + b' = \int_0^{T_i} c_i \, dT + b' \equiv h_i(T_o). \]

(2.35)

Taking the enthalpy of ice at 0°C, \( h_i(T_o) \), as the particular reference energy level and subtract it from the specific enthalpy, one can now redefine the specific total heats \( h \) as

\[ h_v(T_v) = \int_0^{T_v} c_{p_v} \, dT + l_v(T_v) \equiv \vartheta(T_v) + l_v(T_v), \]
\[ h_w(T_w) = \int_0^{T_w} c_w \, dT + l_f(T_w) \equiv \vartheta(T_w) + l_f(T_w), \]
\[ h_i(T_i) = \int_0^{T_i} c_i \, dT \equiv \vartheta(T_i), \]

(2.36)

where \( \vartheta \) is defined as the sensible heat integrated from 0°C. The total heats \( H_v, H_w, \) and \( H_i \) are then the specific heats multiplied by the mass.
2.2. Liquid-Phase Microphysics

The thermodynamic theories for phase-changes as discussed in the previous section provide the basis for describing the growth of cloud particles by vapor diffusion. The earlier part of this section will be devoted to the equilibrium states of droplets and their growth kinetics. The latter part of this section will discuss the further growth of droplets through hydrodynamic interactions.

2.2.1. Theory of Deliquescence and the Activation of Cloud Drops

The Köhler equation discussed previously states that the saturation vapor pressure over the drop surface can be depressed by the solute effect or enhanced by the curvature effect. The water vapor saturation ratio over a solution drop is defined as

\[ S \equiv \frac{e_s(a, a_w, T)}{e_s(\infty, 1, T)}. \]  

(2.37)

This equilibrium saturation ratio can be plotted as a function of the drop radius at different solute content, as shown in Figure 2.2. This family of curves with different solute content is often called the Köhler curves. The particular family of Köhler curves plotted in Figure 2.2 pertains to solution drops with various amount of (NH$_4$)$_2$SO$_4$ (ammonia-sulfate), with appropriate formulas for the solution density $\rho_w$, solution surface tension $\sigma_{wa}$, and van't Hoff's factor $i_s$ from Fitzgerald (1974). Drops in the atmosphere may either grow or evaporate depending on their status on the diagram relative to the environmental humidity. For a drop of a certain size, condensation (evaporation) will occur if the environmental saturation ratio $S_\infty$ is higher (lower) than the equilibrium saturation ratio indicated by the point on the Köhler curve at the same drop size. During
condensation (evaporation), the position of the drop moves toward the right (left) on the diagram until it meets the Köhler curve. In the case of evaporation, the drops will eventually intercept the Köhler curve to reach equilibrium and stay in their haze state. For condensation, drops will reach their haze state only at the sizes where the slope of the Köhler curve is positive. This happens when the environmental saturation ratio is below the maximum on the Köhler curve (the critical saturation ratio $S^*$) and the drop size is smaller than the critical radius $r^*$ that corresponds to $S^*$ on the Köhler curve. At sizes larger than the critical radius $r^*$, where the slope of the Köhler curve is negative, drops are in their unstable states and can be activated into cloud drops.

![Köhler curves](image)

**Figure 2.2:** The Köhler curves: variation of the equilibrium saturation ratio with drop radius for solution drops formed from ammonia-sulfate particles of dry radius $r_{AS} = 0.001, 0.01, 0.1$ and $1 \mu m$ at $0 ^\circ C$. 
When the environmental saturation ratio $S_\infty$ (or relative humidity) decreases, haze particles must reduce in size to maintain the equilibrium. The reduction in size is achieved by the evaporation of water (assuming the solute is non-volatile), so resulting in higher solute concentration. However, due to the finite solubility, solute concentration cannot increase indefinitely and the solute will eventually precipitate out. The solid phase may appear when the environmental saturation ratio $S_\infty$ is below a value that may be called the *dehydration point* $S_{\text{dehyd}}$. The solute activity then becomes constant and can no longer change to offset the increasing curvature effect during the continuous evaporation of the haze drops. The haze particle is then thermodynamically unstable such that all water will evaporate. Figure 2.3 shows the Köhler curves after including the solubility limitation. The Köhler curves are at constant offsets to the Kelvin curve when $S_\infty < S_{\text{dehyd}}$ until the particle reaches its dry size. Let us examine the process from an opposite direction of the change of relative humidities. A dry particle is thermodynamically unstable once the relative humidity reaches the *deliquescence point* $S_{\text{deliq}}$ (see Figure 2.3). With a relative humidity above $S_{\text{deliq}}$, the particle will deliquesce into a solution drop. Note that both of the thermodynamically unstable regions on the Köhler curve (deliquescence stage and activation stage) occur where the slope of the curve is negative.

The *deliquescence point* can be derived by letting the radius in the curvature term in the Köhler equation be the radius of the dry particle. Thus,

$$S_{\text{deliq}} = a_w^* \exp\left(\frac{2\sigma_{w/a}}{\rho_s R_s T a_s}\right)$$  \hspace{1cm} (2.38)

where, $\rho_s$ and $a_{AS}$ are the density and radius of the dry particle, $\sigma_{w/a}$ is the surface tension between air and the solution, and $a_w^*$ is the water activity in the solute-saturated solution:
Figure 2.3: Modified Köhler curves which include the theory of deliquescence. $S_{\text{dehyd}}$ is the dehydration point, $S_{\text{deliq}}$ is the deliquescence point, $S_{\text{dehyd,b}}$ is the bulk dehydration point, and $S_{\text{dehyd,s}}$ is the spontaneous dehydration point. Curves A and B are for $r_{AS}$ of 0.01 and 0.1 µm, respectively. The gray lines are the traditional Köhler curves below the equilibrium dehydration point and the thin-dotted line connects the deliquescence part of the curves.
\[ a_w^* = \frac{n_w}{n_w + i_s n_s}, \quad (2.39) \]

where \( n_s \) and \( n_w \) are the total number of moles of solute and water in the solution, and \( i_s \) is the van't Hoff dissociation coefficient. The activity of water can be expressed in terms of the solubility:

\[ a_w^* = \frac{1 - Q_s(T)}{1 - Q_s(T) + i_s Q_s(T)}. \quad (2.40) \]

At the dehydration point, all the solute is dissolved in the solution and has a concentration exactly the same as the solubility, so that:

\[ Q_s(T) = \frac{n_s}{n_s + n_w} = \frac{1}{1 + \frac{n_w}{n_s}} = \frac{1}{1 + \frac{M_s (r_{w,\text{equil}}^3 \rho_w - r_s^3 \rho_s)}{M_w r_s^3 \rho_s}}, \quad (2.41) \]

where \( n_w \) and \( n_s \) are the total moles of water and solute in the drop, \( r_{w,\text{equil}} \) is the equilibrium radius of haze, \( \rho_w \) the density of the solution, \( r_s \) and \( \rho_s \) the radius and density of the dry particle, and \( M_w \) and \( M_s \) the molecular weight of water and solute.

The equilibrium haze size is thus

\[ r_{w,\text{equil}} = r_s \left\{ \frac{\rho_s}{\rho_w} \left[ \frac{M_w}{M_s} \left( \frac{1}{Q_s(T)} - 1 \right) + 1 \right] \right\}^{1/3}, \quad (2.42) \]

which can be insert back into (2.40) to get

\[ S_{\text{dehyd}} = a_w^* \exp \left( \frac{2 \sigma_{\text{w/a}}}{\rho_w R_T r_{w,\text{equil}}} \right). \quad (2.43) \]

By neglecting the curvature term in the above equation, we get the bulk dehydration point:
As can be seen from Figure 2.3, both $S_{\text{dehyd}}$ and $S_{\text{dehyd}}$ approaches $S_{\text{dehyd,b}}$ at large $r_s$.

Similar to the supersaturation of water vapor in the air, the solution may also become supersaturated especially when no heterogeneous nuclei exist in the solution. Therefore, even when $S_\infty$ is less than $S_{\text{dehyd}}$, haze particles may stay in a meta-stable state with a solute concentration exceeding the solubility limitation until $S_\infty$ drops below the spontaneous dehydration point $S_{\text{dehyd,s}}$, at which point homogeneous nucleation of solute takes place. As mentioned in the previous section, the spontaneous dehydration occurs when the drop concentration is about $Q_s(T)+0.29$ for ammonia-sulfate solution. The spontaneous dehydration process is very similar in concept to the so-called homogeneous freezing point of water.

The temperature dependence of the solubility may play an important role in the ice-phase cloud microphysics. Figure 2.4 shows the solubility and the corresponding thermodynamic dehydration point $S_{\text{therm}}$ as a function of temperature. Low solubility at low temperatures means a small Raoult effect. The deliquescence point $S_{\text{deliq}}$ may exceed ice saturation, or even water saturation, at low temperatures for small $r_{AS}$. Therefore, in the cold region of clouds, interstitial particles may exist in their dry state instead of in their haze state. Beard (1992, to be published in Atmospheric Physics) proposed that ice nuclei could be created from the residue of evaporated cloud droplets. It is possible that some of these dry interstitial particles may also have the right structure for acting as ice-forming nuclei. Because these dry particles often exist in high number concentrations compared with the typical ice particle concentrations in the atmosphere, even a small fraction of these dry particles being able to act as ice nuclei would be significant. From equation (2.42), we can estimate that haze particles shrink about 30% in size during the dehydration process ($r_{w,equil} \approx 1.5 r_{AS}$). For particles smaller than the
Greenfield gap (a minimum in the collection efficiencies), the collection efficiency of interstitial particles by large cloud particles increases with decreasing particle size. Therefore, the dehydration process may suddenly enhance the removal of interstitial aerosols in the clouds. Because it involves the change of particle phase, the dehydration process may also be important for the formation of clouds and the heterogeneous chemistry occurring in the stratosphere.

Figure 2.4: Solubility and the dehydration point as a function of temperature for ammonia-sulfate solution.
Cloud drops must first grow by condensation before they have the chance to grow by collection and form precipitation. Condensation is a gas diffusion process that requires a vapor density gradient between the drop surface and the surrounding air. Under typical conditions, neighboring droplets are sufficiently far apart that we may regard each one as growing at the expense of an infinite field of vapor. It follows that an analogy exists between the field of vapor density $\rho$ around a cloud particle and the field of the electrostatic potential $V$ existing around a charged conductor. Such an analogy was introduced as early as the late 19th Century by Stefan (1873) and Maxwell (*Encyclopædia Britannica*, 9th ed., 1878) to study the condensation/evaporation process in relation to observed wet bulb temperatures. Jeffreys (1918) also introduced the solution of the steady-state diffusion equation, which was applied to the growth of droplets by Houghton (1950). With the electrostatic analogy, *Fick’s first law* for the vapor density flux can be expressed as:

$$\vec{J} = -D_v \nabla \rho ,$$

(2.45)

where $D_v$ is the diffusivity of water vapor in air and $\rho$ is the local vapor density. Applying the continuity equation for $\rho$, with the assumption of incompressible air flow, we have *Fick’s second law* (or the *diffusion equation*):

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot \vec{J} = D_v \nabla^2 \rho ,$$

(2.46)

where $D_v$ is assumed to be independent of position. Since the characteristic time for vapor diffusion to a drop of radius $r$ (Hidy and Brock, 1970, Section 4.2),

$$\tau_{\text{diff}} = \frac{r^2}{\pi D_v} ,$$

(2.47)
is usually much smaller than the time for significant changes in vapor density, we may make a quasi-steady state assumption, so that

\[ \nabla^2 \rho = 0. \tag{2.48} \]

With the boundary conditions of \( \rho = \rho_\infty \) at \( r = \infty \) and \( \rho = \rho_w \) at the drop surface \( (r = a) \), this (Laplace’s) equation has the following solution

\[ \rho(r) = \rho_\infty - \Delta \rho \frac{a}{r}, \tag{2.49} \]

where \( \Delta \rho = \rho_\infty - \rho_w \) is the excess vapor density. The mass flux over the surface \( A \) of the drop, based on Gauss’ law and Fick’s law of diffusion, is given as

\[ \frac{dm}{dt} = \int_A \nabla \rho \cdot \hat{n} \, dA = 4\pi C \Delta \rho, \tag{2.50} \]

where \( \hat{n} \) is the outward unit vector pointed normal to the surface and \( C \) is the electrostatic capacitance, which equals to the radius \( a \) for a spherical particle. The above diffusional growth theory is sometimes called the two-stream Maxwellian kinetic theory (Robinson and Scott, 1981).

1. Heat Transfer Equation

Besides mass transfer, the diffusional growth of droplets also involves the transfer of heat following the equation

\[ \frac{dH_w}{dt} = \left. \frac{dH_w}{dt} \right|_{\text{cond}} + \left. \frac{dH_w}{dt} \right|_{\text{diff}}, \tag{2.51} \]

which describes the two main sources of heat: (1) heat from the air by conduction, viz.,

\[ \left. \frac{dH_w}{dt} \right|_{\text{cond}} = 4\pi r k_a (T_\infty - T_w), \tag{2.52} \]
and (2) the total heat (defined in Section 2.1) that comes with the water vapor:

\[
\frac{dH_w}{dt}_{\text{diff}} = h_v \frac{dm_w}{dt}_{\text{diff}}.
\] (2.53)

Here, \(m_w\) and \(T_w\) are the mass and temperature of the drop, \(k_a\) is the heat conductivity of air; and \(\frac{dm_w}{dt}_{\text{diff}}\) is the mass growth rate from (2.50). Note that the electrostatic analogy, as suggested by Maxwell, can also be applied in the derivation of the heat conduction term.

2. Modification Factors

Equations (2.50) and (2.51) together describe the diffusional growth of droplets in an idealized situation. In reality, these rates should be modified by the following factors: (1) ventilation effect, (2) gas-kinetic effects, and (3) source and sink proximity effects (Miller and Young, 1979). The modified mass growth equation is given generally by

\[
\frac{dm}{dt} = 4 \pi r D_v \Delta \rho f_v f_{kin} f_{prx},
\] (2.54)

where \(f_v, f_{kin},\) and \(f_{prx}\) account for the crystal’s ventilation, surface kinetic, and the proximity effects for mass. The modified conduction heating equation is

\[
\frac{dH_w}{dt}_{\text{cond}} = 4 \pi r k_a \frac{\Delta T}{T_d} f_h f_{kin}^* f_{prx}^*,
\] (2.55)

where \(f_h, f_{kin}^*,\) and \(f_{prx}^*\) account for the drop’s ventilation, surface kinetic, and the proximity effects for heat.

Ventilation contributes to the drop growth by enhancing the vapor flux and the rate at which heat is removed from the drop, the buildup of which would otherwise hinder the growth. This effect is potentially important for large drops that attain appreciable fall velocities. The empirical expression for \(f_v\) and \(f_h\), given by Beard and Pruppacher (1971), is listed in Appendix A.
If the size of the drop is not much greater than the mean free path of the water vapor molecules, diffusion theory predicts mass and heat transfers greater than those that can be allowed according to the kinetic treatment. The mass-transfer correction factor for a spherical particle is given as (Fuchs, 1959)

\[
    f_{\text{kin}} = \left[\frac{r}{r + \Delta} + \frac{D_v}{\alpha_c r} \sqrt{\frac{2\pi}{R_v T}}\right]^{-1}
\]  

(2.56)

where \( r \) is the radius of the particle; \( \Delta \sim 0.1 \, \mu m \) is the thickness of a boundary layer within which the molecules are transferred by the kinetic process (i.e., without molecular collision) and outside of which the transfer is according to classical diffusion theory; \( D_v \) is the diffusivity of water vapor in air; \( R_v \) is the specific gas constant for water vapor; and \( \alpha_c \) is the condensation coefficient. The correction factor for the heat transfer is in a similar form but has a value very near unity (Miller and Young, 1979).

The derivation of the mass and heat equations that applied the electrostatic analogy assumes no sources or sinks except at the particle’s surface and at infinity. In reality, cloud particles are situated in an environment containing other particles that compete for the available water vapor. This proximity effect is typically small and is not treated here.
2.2.3. Hydrodynamic Interactions

Under normal atmospheric conditions, the condensational growth process alone is usually not sufficient to produce precipitation-size drops (i.e., raindrops). Raindrops are formed either through the melting of ice particles (Bergeron, 1935; Findeison, 1938) or by means of collision-coalescence (Langmuir, 1948; Telford, 1955). The latter is called the warm-rain process. Müller (1928) derived a continuous form of the scalar transport equation (also referred to as the coagulation equation, the collection equation, the kinetic equation, the stochastic coagulation equation and, most often, the stochastic collection equation) for the particle-capture process:

\[
\frac{\partial n(v)}{\partial t} = -n(v) \int_0^{\infty} K(v, u) n(u) du + \frac{1}{2} \int_v^{\infty} K(v-u, u) n(v-u) n(u) du ,
\]

where \(u\) and \(v\) are the masses of the particles, \(n\) the time varying particle size (mass) density function, and \(K(u, v)\) the particle interaction kernel. Telford (1955) introduced the scalar transport equation to the drop collection problem. The first term on the right-hand-side denotes the loss of drops with mass \(v\) due to the gain of mass by collecting other drops, while the second term represents the creation of drop with mass \(v\) due to the coalescence of two drops with mass \(u\) and \(v-u\). The interaction kernel \(K\) is defined as

\[
K(u, v) = E_c(u, v) \pi(r_u + r_v)^2 \left| V_{\infty, u} - V_{\infty, v} \right| ,
\]

where \(E_c(u, v)\) is the collection efficiency, \(r_u\) and \(r_v\) are the drop radii, and \(\left| V_{\infty, u} - V_{\infty, v} \right|\) is the absolute difference in velocity between the two drops. The collection efficiency is composed of two parts: \(E_c = E_{\text{colli}} E_{\text{coal}}\). The first part, the collision efficiency \(E_{\text{colli}}(u, v)\), is the probability for a drop to collect a distant droplet that lies within its geometrical sweepout cross section \(\pi(r_u + r_v)^2\). The collision efficiencies can be determined either by
laboratory measurement or from theoretical calculation. Unfortunately, there are substantial differences between the current theories and experiments. In this study, the collision efficiencies from theoretical calculations are used because of their completeness and ability to include the turbulence effect. More details on the values of the collision efficiencies will be given in Section 3.6.1.1.

Not all drops will coalesce upon collision. The drops may also breakup into many small drops or simply bounce off each other. The second part of the collection efficiency $E_{\text{coal}}$ is called the coalescence efficiency. By also defining the breakup and rebound efficiencies as $E_{\text{brk}}$ and $E_{\text{reb}}$, we have $E_{\text{coal}} + E_{\text{brk}} + E_{\text{reb}} = 1$. These three results of collision will be discussed separately in the following sections.

### 2.2.3.1. Collision-Coalescence

The drop coalescence and breakup problems are so complex that they can not be handled well with existing theoretical techniques, certainly not as well as done for the collision efficiencies. Among various experimental studies, the measurements by Low and List (1982a) for drops falling at terminal speeds are probably the most extensive. They approximated the empirical relationship for the coalescence efficiency by

$$E_{\text{coal}} = a \left[ 1 + \frac{D_S}{D_L} \right]^{-2} \exp \left[ -\frac{b\sigma E_T^2}{S_C} \right], \quad (2.59)$$

$$E_T = E_{\text{cke}} + S_T - S_C, \quad E_{\text{cke}} = \frac{\rho \pi}{12} \frac{D_L^3 D_S^3}{D_L^3 + D_S^3} (V_L - V_S)^2,$$

$$S_T = \pi \sigma (D_L^2 + D_S^2), \quad S_C = \pi \sigma (D_L^3 + D_S^3)^{2/3},$$

where $a = 0.778$, $b = 2.61 \times 10^6 \text{ J}^2 \text{ m}^2$, $D_L$ and $D_S$ are the diameters of the large and small drops, $\sigma$ is the surface tension, $V_L$ and $V_S$ are the terminal velocity of the large and
the small drops, $E_T$ is the total energy of coalescence, $E_{CKE}$ is the collision kinetic energy, $S_T$ is the total surface energy of the incident drops, and $S_C$ is the surface energy of the spherical equivalent of the united drop mass. The data given by Low and List (1982a) is not extensive, but it has been chosen to cover the range most important to rainfall development. Bradley and Stow (1984) have since questioned their interpretation of the results. Although they failed to consider the last four drop pairs in Table 3 of Low and List (1982a), Bradley and Stow claimed that the expression

$$E_C = 1 - 0.67(E_T / S_C)^{0.36}$$

(2.60)
describes the data equally well. By separating the collection efficiency into the collision and coalescence coefficients, the coalescence equation can be written as

$$\frac{\partial h(v)}{\partial t} = \frac{1}{2} \int_0^v K'(v-u,u) E_{coal}(v-u,u) n(v-u) n(u) du$$

$$-n(v) \int_0^v K'(v,u) E_{coal}(v,u) n(u) du,$$

(2.61)

where $K'(v,u) = E_{colli}(v,u) (r_v + r_u)^2 | v - u |$.

### 2.2.3.2. Collision-Breakup

Similar to the collection equation (2.57) in the last section, we can also write down the breakup equation as

$$\frac{\partial h(v)}{\partial t} = \frac{1}{2} \int_0^v \int_\mu \mu n(\mu) n(\eta) K'(\mu, \eta) E_{brk}(\mu, \eta) P(\mu; \mu, \eta) d\eta d\mu$$

$$-\int_0^v \int_\eta \int_\eta \mu n(v) n(\eta) K'(v, \eta) E_{brk}(\mu, \eta) P(\mu; v, \eta) d\mu d\eta,$$

(2.62)
Here, \( P(\nu; \mu, \eta) \) is the number of fragments of mass \( \nu \) per collision resulting from breakup of drops with masses \( \mu \) and \( \eta \). The collision-breakup process adds another fold to the complexity of the hydrodynamic interactions because of the distribution of the drop fragments. According to the geometric shape assumed immediately after impact, Low and List (1982a) stratified the type of breakup into filament, sheet and disk configurations. An effort was also made to parameterize the fragment size distribution (Low and List, 1982b; List et al., 1987). However, their description is not well organized and has some errors in the formulas. The following is a reorganization and summary of their scheme. The parameterization scheme can be summarized in three parts: (1) breakup probability for each breakup type, (2) total number of fragments produced in one collision, and (3) the probability function for the fragment drop distribution.

1. **Breakup Types and Their Probabilities**

   The breakup probability of each breakup type is determined by the collision kinetic energy \( E_{\text{CKE}} \). For values of \( E_{\text{CKE}} \) less than \( 8.93 \times 10^{-7} \) J, filament breakup is the only breakup mode. Otherwise, the probability of filament breakup is

   \[
   Q_f = 1.11 \times 10^{-4} E_{\text{CKE}}^{-0.654} \; ;
   \]  

   the probability of sheet breakup is

   \[
   Q_s = 0.685 \{1 - \exp[-1.63(W_2 - W_0)]\} \quad \text{for } W_2 \geq W_0 = 0.86
   \]

   \[
   = 0 \quad \text{otherwise},
   \]

   with \( W_2 = E_{\text{CKE}} / S_f \); and the probability of disk breakup is

   \[
   Q_d = 1 - Q_f - Q_s .
   \]  

   Note that \( Q_s \) should be set as \( 1 - Q_f \) when \( Q_s + Q_f > 1 \).
2. Total number of Fragments

The total number of fragments for filament breakup, including the two parent drops, is formulated as

\[
N_{f,i} = \left[ -2.25 \times 10^4 (D_L - 0.403)^2 - 37.9 \right] D_S^{2.5} + 9.67 (D_L + 0.170)^2 + 4.95
\]

for \( D_S \geq D_0 \),

\[
N_{f,2} = a D_S^b + 2 \quad \text{for } D_S < D_0 , \quad (2.66)
\]

where \( D_L \) and \( D_S \) are in cm, \( a = 1.02 \times 10^4 \), \( b = 2.83 \) and \( D_0 = \left[ \frac{N_{f,i} - 2}{a} \right]^{1/b} \). The total number of sheet breakup events is

\[
N_s = 5 \text{erf} \left( \frac{S_T - 2.53 \times 10^{-6}}{1.85 \times 10^{-6}} \right) + 6 , \quad (2.67)
\]

and for disk breakup the number is

\[
N_d = \max(297.5 + 23.6 \ln E_{\text{KE}}, 2) . \quad (2.68)
\]

In the case of sheet and disk breakup, the smaller parent drop is no longer recognizable among the fragments. In filament breakup, both parent drops were observed to survive with part of their mass ripped out and to form fragments during collision. Therefore, \( N_s \) and \( N_d \) are always \( \geq 2 \), while \( N_f \geq 3 \).
3. Drop Distribution Function

The probability function of the parent drops is assumed to be a normal distribution in the form of

\[ P(D) = H \exp \left( -\frac{1}{2} \left( \frac{D - \mu}{\sigma} \right)^2 \right) = \frac{N}{\sqrt{2\pi\sigma}} \exp \left( -\frac{1}{2} \left( \frac{D - \mu}{\sigma} \right)^2 \right). \] (2.69)

Here, \( H, \mu, \sigma \) and \( N \) are the height, mode, standard deviation and total number of the distribution, respectively. Since there is only one of each parent drop, \( N \) simply equals one. The probability function of the fragment drops is assumed to be log-normal, thus,

\[ P(\ln D) = \frac{H}{D} \exp \left( -\frac{1}{2} \left( \frac{\ln D - \mu}{\sigma} \right)^2 \right) = \frac{N_x}{D\sqrt{2\pi\sigma}} \exp \left( -\frac{1}{2} \left( \frac{\ln D - \mu}{\sigma} \right)^2 \right). \] (2.70)

Now, \( N_x \) is the total number of fragments. For filament breakup, \( N_x = N_f - 2 \) since both parent drops exist. For sheet and disk breakup, \( N_x = N_s - 1 \) and \( N_x = N_d - 1 \), respectively. Before giving the functional form of the height, mode and standard deviation for each distribution, let us first examine the integration of the distribution. The number of drops between sizes \( D_1 \) and \( D_2 \) is

\[ N(D_1, D_2) = \int_{D_1}^{D_2} P(D)dD = \frac{1}{2} \left[ \text{erf}(x_2) - \text{erf}(x_1) \right], \] (2.71)

where \( x_i = \frac{D_i - \mu}{\sqrt{2}\sigma} \). The total mass in the same interval is expressed as

\[ W(D_2, D_1) = \int_{D_1}^{D_2} \frac{\pi D}{6} P(D)dD \] (2.72)

\[ = \frac{\pi D}{6\sqrt{\pi}} \left\{ -c_2 \exp(-x_2^2) + c_1 \exp(-x_1^2) + A[\text{erf}(x_2) - \text{erf}(x_1)] \right\}, \]

where
\[ c_i = \sqrt{2\sigma} \left[ \sigma^2 (x_i^2 + 1) + \frac{3}{2} \mu (\sqrt{2} \sigma x_i + \mu) \right], \text{ and } \quad A = \sqrt{\pi \mu} \left( \sigma^2 + \frac{\mu^2}{2} \right). \]

These derivations can be found in Valdez and Young (1985), but notice there is an error in their formula for \( c_i \). Similarly, the integrated number and total mass for the log-normal distribution are

\[
N(D_1, D_2) = \frac{N_X}{2} \left[ \text{erf}(y_2) - \text{erf}(y_1) \right], \quad \text{and} \quad (2.73)
\]

\[
W(D_1, D_2) = \frac{\pi \rho}{6} \frac{N_X}{2} \exp \left( -\frac{9}{2} \sigma^2 + 3\mu \right) \left[ \text{erf}(y_2 - \frac{3\sigma}{\sqrt{2}}) - \text{erf}(y_1 - \frac{3\sigma}{\sqrt{2}}) \right], \quad (2.74)
\]

where

\[
y_i = \frac{\ln D_i - \mu}{\sqrt{2}\sigma}.
\]

Note that the total number of fragments \( N_X \) is already included in the formulas. In order to determine the parameters \( H, \mu \) and \( \sigma \), Low and List (1982b) measured some of the parameters and utilized the above formulas to determine the others. If we first consider the parent drops (normal distribution), the heights were measured as

\[
H_{f,L} = 50.8 D_L^{0.718}, \quad H_{f,S} = 4.18 D_S^{1.17},
\]

\[
H_{s,L} = 100 \exp(-3.25D_3), \quad (2.75)
\]

\[
H_{d,L} = 1.58 \times 10^{-5} E_{\text{CKE}}^{-1.22},
\]

and the modes were found to be

\[
\mu_{f,L} = D_L, \quad \mu_{f,S} = D_S,
\]

\[
\mu_{s,L} = D_L, \quad (2.76)
\]

\[
\mu_{d,L} = D_L \{ 1 - \exp[-3.70 (3.10 - E_{\text{CKE}} / S_C)] \}.
\]
The standard deviation $\sigma$ can be derived easily from the above two parameters. However, there are some problems caused by the experimental size limit $D^* = 0.01$ cm. The total number of drops is actually $N(D_{\text{coal}}, D^*)$, where $D_{\text{coal}}$ is the maximum possible size (i.e., the coalesced drop size). Therefore,

$$1 = N(D_{\text{coal}}, D^*) = \frac{1}{2} \left[ \text{erf} \left( \frac{D_{\text{coal}} - \mu}{\sqrt{2}\sigma} \right) - \text{erf} \left( \frac{D^* - \mu}{\sqrt{2}\sigma} \right) \right].$$  \hspace{1cm} (2.77)

Since $D^* \ll \mu$ for parent drops, we can simplify the above equation as

$$1 = \frac{1}{2} \left[ \text{erf} \left( \frac{D_{\text{coal}} - \mu}{\sqrt{2}\sigma} \right) + 1 \right]$$  \hspace{1cm} (2.78)

and use $\mu$ to solve for $\sigma$. Note that, from the definition of $H = 1/\sqrt{2\pi}\sigma$, we can easily get $\sigma = 1/\sqrt{2\pi}H$, a result equivalent to using $N(\infty, 0)$ as the total number.

The derivation of the three distribution parameters for the fragment drops (log-normal) is not straightforward. The mode (in cm) of fragment distribution in linear-scale is first measured as

$$D_{f,X} = 0.241 D_S + 0.0129$$

$$D_{s,X} = 0.254 D_S^{0.413} \exp \left[ (3.53 D_s - 2.51)(D_L - D_S) \right]$$  \hspace{1cm} (2.79)

$$D_{f,X} = \exp \left[ (-17.4 D_s - 0.671)(D_L - D_S) \right] D_S.$$

The transformation of the mode from a linear-scale to a log-scale is done by

$$\mu_{l,X} = \ln D_{l,X} + \sigma_{l,X}$$  \hspace{1cm} (2.80)

where the subscript "i" is the breakup type, and $X$ denotes fragments. Low and List provided the probability function value at the mode:
\[
P(D_{f,x}) = 1.68 \times 10^5 D_s^{2.33} \equiv A \quad \text{for } D_S \leq D_o
\]

\[
= [43.4(D_L + 1.81)^2 - 159.0]D_s^{-1} - 3870(D_L - 0.285)^2 - 58.1 \equiv B
\]

for \( D_S \geq 1.2D_o \)

\[
= \alpha A + (1-\alpha) B \quad \text{for } D_o < D_S < 1.2D_o
\]

\[
P(D_{s,x}) = 0.23D_S^{-3.93}D_L^{14.2} \exp(-17.2D_S)
\]

\[
P(D_{d,x}) = 8.84D_S^{-2.52}(D_L - D_S)^{0.007D_s^{254}}, \quad (2.81)
\]

where \( \alpha = (D_S - D_o) / (0.2D_o) \). Then, from the expression of the probability function at the mode

\[
P(D_{i,x}) = \frac{H}{D_{i,x}} \exp\left(\frac{-\sigma^2}{2}\right) \quad (2.82)
\]

and the expression for total number

\[
N_x = H\sigma \left[ \frac{\pi}{2} \left[ \text{erf}\left( \frac{\ln D_{coal} - \mu_{i,x}}{\sqrt{2}\sigma} \right) - \text{erf}\left( \frac{\ln D^* - \mu_{i,x}}{\sqrt{2}\sigma} \right) \right] \right]
\]

\[
\approx H\sigma \left[ \frac{\pi}{2} \left[ 1 - \text{erf}\left( \frac{\ln D^* - \mu_{i,x}}{\sqrt{2}\sigma} \right) \right] \right], \quad (2.83)
\]

the parameters \( H, \mu_{i,x}, \) and \( \sigma \) can be calculated by iteration. However, the above equations are sometimes ill-behaved and the iteration may fail to converge. One should use a safe iterative procedure, such as the "method of false position" of Brown (1989), to ensure the convergence of the solution.
4. Mass Conservation

The parameterization of Low and List (1982b) was designed to provide a general distribution function that would fit closely the data from laboratory measurement. With the given parameters, however, the scheme fails to conserve mass. As pointed out by Valdez and Young (1985), the error can sometimes be as much as 30%. Various methods have been used to deal with this problem, such as the "clipping and scaling" of Valdez and Young (1985) and the linear adjustment in the breakup coefficients of Brown (1989). Yet, these modification schemes lack physical interpretation. If it may be assumed that the normal and log-normal distributions are realistic, the error in total mass should be a result of experimental inaccuracy in the parameters $H$, $\mu$, or $\sigma$. One can imagine that it would be easier to get a correct number count than to accurately measure the size of the drop fragments. We can thus assume there to be no error in $H$ and $\sigma$ and that all the error is in $\mu$. If we integrate equation (2.74) over the whole spectrum (from $D = 0$ to $\infty$ or $x = -\infty$ to $\infty$), we can derive the total mass:

$$W_{\text{tot}} = \frac{\pi D}{6} N \mu (3\sigma^2 + \mu^2).$$

(2.84)

Suppose that the total mass and mode of the actual spectrum are $W'$ and $\mu'$, and the calculated mass $W_{\text{tot}}$ is $Q$ times of $W'$. We then have

$$\mu (3\sigma^2 + \mu^2) = Q \mu (3\sigma^2 + \mu^2),$$

(2.85)

and $\mu$ can be solved from this cubic equation. Similarly, for the log-normal distributions, the total mass can be expressed as

$$W_{\text{tot}} = \frac{\pi D}{6} N \exp\left(\frac{Q}{2} \sigma^2 + 3\mu\right),$$

(2.86)

and we have
The actual mode is thus

$$\mu' = \mu + \frac{\ln Q}{3}.$$  \hspace{1cm} (2.88)

The conservation of mass achieved by shifting the mode can be performed on the
distribution of either the parent drops or the fragments. Note that, in deriving the total
mass, we set the lower limit to be $D = 0$, not $D = D_0$. This might cause a small error in
deriving the actual mode and does not conserve mass exactly. Without using the
calculation above, we can also utilize the "bin-shift" numerical technique that will be
discussed in Section 3.1 to shift the whole spectrum. The bin-shift method guarantees
the conservation of mass.

5. **Solute Redistribution**

The Low and List scheme does not tell us whether the mass of fragment drops is
from either parent drops or both. The information of mass redistribution is important
when we need to know the solute concentration in the drops. In this study, it is assumed
that when one of the parent drops gains mass, its does not contribute any of its original
mass to the fragment drops. Thus, the mass of the fragment drops must be from the
other parent drop, which also provides mass to the first parent drop. If both of the
parent drops lose mass, they do not gain any mass or solute from the other, and their
original concentrations are preserved. The fragment drops will have the same
concentration as those in the mixture of the masses that were stripped away from the
parent drops.
6. **A Stereo View of the Breakup Distribution Function**

The stereograph shown in Figure 2.5 is an example of the breakup distribution for a large drop of $D_L = 4.09$ mm interacting with small drops of various diameter $D_S$. The large drop is indicated by the ridge on the left that parallel to the $D_S$-axis; the small drop is in the diagonal direction from the lower right toward the center of the graph. For this particular value of $D_L$, both parent drops remain essentially intact for $D_S$ less than about 0.5 mm. As the small drop becomes larger, a population of fragment drops is produced as shown by the broad, third ridge just to the right of the ridge of the small parent drop. For $D_S$ greater than about 1 mm, the remaining of the smaller parent drop is no longer recognizable and is essentially a part of the fragment drop population. Note that the saw-toothed shape for the distribution of the small parent drop is artificial and should be a more continuous ridge.

![Figure 2.5: A stereo view of the breakup size distribution $D_X$ for large drop with diameter $D_L = 4.09$ mm colliding with small drop of various diameter $D_S$.](image-url)
2.2.3.3. Rebound

It has been generally accepted that once the surfaces of two drops are in contact, coalescence will proceed at least temporarily (Pruppacher and Klett, 1980, p.488). The situation that the drops collide without coalescence or breakup occurs when a film of air is trapped between the drops and serves to keep them apart. Comprehensive observations on drop rebound versus coalescence of breakup have been reported by Park (1970). Foote (1975) also studied the rebound problem by numerically solving the fluid motions in the colliding drops and in the air. However, no attempt was made to extract a rebound efficiency from these studies. It is, therefore, assumed that \( E_{\text{reb}} = 0 \), and \( E_{\text{coal}} + E_{\text{brk}} = 1 \) in this study. A situation similar to the rebound occurs when two colliding drops join temporarily then breakup into two drops. The drop masses, in this case, may have been redistributed between the two parent-drops during the process. In the procedures for determining the breakup probability function discussed previously, one can assume such "disruptive" rebound occurs when one find that \( N_X \leq 0 \) or \( P(D_{i,X}) \leq 0 \).

2.2.3.4. Spontaneous Breakup

The three collisional processes discussed previously are actually "three-body" interactions that involve two drops and the air. A drop may also breakup spontaneously without interacting with other drops. This spontaneous breakup process involves only two bodies, and was thought to be the equalizing factor that works against the coalescence and maintains the exponential raindrop size spectra. Wind tunnel measurements by Pruppacher and Pitter (1971) have shown that the largest stable drops in still air have spherical equivalent radii of about 4.5 mm. However, raindrops are
rarely observed to have radii greater than 1 to 2 mm. Evidence suggests that raindrops will undergo collisional breakup long before they have the chance to grow large enough to break up spontaneously. Nevertheless, giant drops larger than 3 mm in radius have been observed in very heavy rain (Mason and Andrew, 1960; Beard et al., 1986; and Rauber et al., 1991). The melting of large ice particles and the shedding of liquid water during the wet growth of hailstone may also produce very large drops, especially when they fall in regions of very low drop number density (e.g., in strong updraft of below cloud base). Thus, the spontaneous breakup is included in this study to cover these situations. An upper limit of 4.5 mm is set as the largest stable drop size. Any drop that exceeds this size, either because it grew by coalescence or arose from the melting of ice, is assumed to break up spontaneously. The breakup size distribution follows the exponential formula given by Srivastava (1971):

\[ P(R, r) = \frac{ab}{R} \exp\left(-\frac{b}{R}r\right) , \]  

(2.89)

where \( P \) is the probability of producing a drop of radius \( r \) from disintegrating a parent drop with radius \( R \). The slope \( b \) of the log-linear distribution function is about 7 according to Komabayasi (1965), while the constant \( a \) can be determined by the condition of mass conservation:

\[ \frac{4\pi}{3} R^3 = \int_{r_o}^{r_1} \frac{ab}{R} \frac{4\pi}{3} r^3 \exp\left(-\frac{b}{R}r\right) dr , \]

(2.90)

where \( r_o \) and \( r_1 \) are the lower and upper limits of fragment drop size. The above integration gives

\[ a = \frac{b^3}{f\left(-\frac{b}{R}r_1\right) - f\left(-\frac{b}{R}r_o\right)} , \]

(2.91)
with the function $f$ expressed as

$$f(x) = \exp(x)[x^3 - 3x^2 + 6x - 6].$$

(2.92)

Srivastava (1971) used the original drop size $R$ as the upper limit and zero as the lower limit, which gives

$$a = \frac{b^3}{6 - \exp(-b)(b^3 + 3b^2 + 6b + 6)} = 62.3.$$  

(2.93)

However, there are some difficulties associated with these two limits. First, some drops are still in the unstable-size regime ($4.5\text{ mm} < r < R$). Also, a large number of drops with unreasonably small sizes may exist according to the exponential distribution function. Thus, it is necessary to put proper limits on the fragment drop sizes. The upper size limit of the fragment drop, $r_1$, is taken as the maximum stable drop size (4.5 mm) while the lower limit $r_0$ can be taken as the same lower limit for collision breakup (0.05 mm).
2.3. Ice-Phase Microphysics

Ice particles tend to acquire water mass more rapidly than liquid drops do by either vapor diffusion or accretion of small droplets. Thus, the existence of ice particles helps the initiation of precipitation, especially in continental air masses. The structure of this section is similar to that for the liquid-phase microphysics in the previous section. We will first see the equivalent of the drop activation -- the nucleation of ice particles, following by their diffusional growth. Ice can also experience hydrodynamic collection similar to the liquid-phase process except that ice can collect both droplets and other ice particles. We will also take a look at the melting, shedding, and secondary generation of ice particles. Special attention is paid to the determination of the shape of ice particles for each growth process.

2.3.1. Ice Nucleation

The nucleation of ice particles is much more complicated than its liquid-phase counterpart -- the activation of cloud drops. The difference stems from the fact that drops form from haze particles that already exist in the liquid-phase, while the nucleation of ice involves the formation of an entirely new phase. In principle, ice particles can be generated in clouds through the direct transformation of water vapor into ice, a process that may be termed homogeneous deposition nucleation. However, heterogeneous nucleation, whereby ice particles are formed on existing foreign particles called ice nuclei, is more common in the troposphere. Let us first review the nature and sources of naturally occurring ice nuclei.
Natural ice nuclei (IN) exhibit large variations in both their distributions and compositions. The size distribution of IN, just like other atmospheric particles, varies greatly according to their geographical location and many other natural factors. The IN are usually composed of insoluble materials such as clays (Kumai, 1951) and various organic compounds (Fukuta, 1963). Soluble particles have a tendency to disintegrate upon absorption of water when the environmental humidity is above the deliquescence point, at which point the structural order that is necessary for ice nucleation is lost. Field studies have shown that small Aitken nuclei are considerably less effective than large aerosol particles (AP) in their ability to nucleate ice. Georgii and Kleinjung (1967) demonstrated a high correlation between the concentrations of large AP and IN, with an IN-to-large-AP ratio of 1/400 at -20 °C. There is no correlation between the concentrations of small AP and IN. The effectiveness of the IN decreases with decreasing size for IN smaller than 0.1 μm, and becomes negligible once the particles are smaller than 0.01 μm (Gerber, 1972). However, such size dependence may vary according to the chemical composition and with the modes of nucleation.

Ice forming nuclei exhibit three basic modes of action. In the first, the deposition mode, water vapor is adsorbed directly onto the surface of the IN. In the second, the immersion freezing mode, ice nucleation is initiated from IN immersed in the supercooled drops. In the third, the contact freezing mode, IN initiates the ice phase by contact with supercooled drops. For IN acting in the deposition mode, the effectiveness of nucleation depends on the water vapor supersaturation of the environment. IN acting in the immersion freezing mode tend to be less affected by the size. There is not enough information on the size dependence of IN acting in the contact freezing mode.
From field studies, it is known that the number concentration of IN exhibits variations by factors up to 10 in different geographical locations and in day-to-day variations. Fletcher (1962) showed that the IN concentrations increase exponentially with decreasing temperature, which means more AP can become effective IN at lower temperature. Fletcher gave the effective IN concentration approximation as

\[ N_{IN} = A \exp(-b \Delta T) , \]  

where \( b = 0.6 \, ^{\circ}C^{-1} \), \( A = 10^{-5} \) per liter, and \( \Delta T = T - T_o \) is the deviation of the temperature from \( 0 \, ^{\circ}C \). The typical concentration of effective IN in the atmosphere is about one per liter at \(-20 \, ^{\circ}C \). Combining Fletcher’s formula and the IN-to-large-AP ratio, which is 1/400 at \(-20 \, ^{\circ}C \) as mentioned before, we can estimate the number of large AP to be about 650 per liter (88 per liter for \( b = 0.5 \, ^{\circ}C^{-1} \)). The number of large AP, which is considered as potential IN, is thus assumed to be between 100 and 1000 per liter in this study. Note that it is necessary to specify the total AP concentration to study the in-cloud scavenging of ice nuclei by cloud particles.

Gagin (1972) and Huffman (1973) found that, in contrast to Fletcher’s suggestion, the number concentration of\textit{ effective} IN increases logarithmically with the supersaturation, \( s \), over ice, independent of temperature, according to the relation

\[ N_{IN} = C s_v^k , \]  

where \( C \) and \( k \) are constant. The value of \( k \) varies from 3 in clean areas to about 8 in polluted areas. Note that the temperature dependence in Fletcher’s finding simply reflects the temperature dependence of ice supersaturation at liquid-water saturation (Huffman, 1973). The results from Fletcher and from Gagin and Hoffman should not be considered as indicating the presence of two different mechanisms. Cotton et al. (1986) mistakenly combined the two formulae to form an equation that contains both temperature and supersaturation dependence.
2.3.1.1. Heterogeneous Deposition Nucleation

Schaller and Fukuta (1979) showed that the rates of heterogeneous deposition nucleation depend on the supersaturation over ice $s_i$ at below-water saturations (except at high sub-zero temperatures where a slightly temperature dependence exists). These nucleation rates vary with the composition of the IN. Their results are qualitatively consistent with the experimental studies by Gagin (1972) and Huffman (1973). Fukuta and Schaller (1982) proposed the condensation-freezing nucleation mode for $s_i$ above water-saturation. At such high supersaturations, water tends to first condense onto the ice nuclei to form a liquid film that then freezes. This mode is very similar to the immersion-freezing process (which will be discussed in next section), but occurs over a somewhat different time scale. In contrast to deposition nucleation, the rate of condensation-freezing is mostly temperature dependent. It tends to occur at lower temperatures with a maximum temperature constraint of about -5 to -15°C, depending on the properties of the nuclei. Such temperature dependence also exists in the immersion-freezing process, as indicated by Vali (1968). In this study, we can consider the condensation-freezing as a subset of immersion-freezing process, which will be discussed in later sections.

Our knowledge about deposition nucleation, like all other ice nucleation processes, is far from adequate. Large uncertainties exist in both the theoretical and experimental studies. Any numerical simulation of ice processes at this stage should not be considered as conclusive, rather as tentative. Huffman’s finding of the strong dependence of IN concentration with ice supersaturation can serve as a parameterization of the depositional nucleation process, and is adopted for this study.
The effective IN considered in equation (2.95) are assumed to nucleate immediately. Therefore, the appearance of effective IN is the same as the creation of new ice particles. Expressing (2.95) in a differential form, we have
\[ dN_{\text{ICE}} = dN_{\text{IN}} = C k s_{v,i}^{k-1} ds_{v,i}, \]  
which can be converted into a rate equation in terms of the time rate of change of supersaturation
\[ \frac{dN_{\text{ICE}}}{dt} = C k s_{v,j}^{k-1} \frac{ds_{v,j}}{dt}. \]  

However, equation (2.95) implies a fixed number of ice nuclei, which is determined by the parameters C and k, at a certain supersaturation. This equation alone cannot account for the sources and sinks of the IN. Also, at a given supersaturation, some IN will nucleate into ice instantaneously, but others will take a little bit longer. This means that, for a fluctuating supersaturation, ice nucleation could still occur even if the instantaneous supersaturation had been reached before. To accommodate these problems, we can modify (2.95) into a fractional form by selecting a reference ice-supersaturation \( s_* \), which is at water-saturation at a sufficiently low temperature \( T_* \), so that:
\[ N_* = C s_*^k, \]  
Here, \( N_* \) represents the concentration of total potential IN, which can be considered as equal to the large AP, and \[ s_* \equiv \frac{e_{s,w}(T_*)}{e_{s,i}(T_*)} - 1. \]  
Since \( dN_{\text{IN}} = -dN_* \), equation (2.0) can be normalize by dividing by \( N_* \):
\[ -1 \frac{dN_*}{N_*} = k s_{v,j}^{k-1} \frac{ds_{v,j}}{s_*^{k}} \frac{dt}{dt}. \]

This equation describes the fraction of total IN that becomes effective IN, which is assumed to nucleate immediately, at a certain rate of change of \( s_{v,j} \). Note that the formula
is now independent of the parameter C. However, it is not possible to determine the total \( N_{IN} \) from (2.95), which does not provide an upper limit of \( N_{IN} \). In fact, the original experiment of Hoffman's was done at temperatures between -12 to -20°C (8 to 24% ice-supersaturation), and does apply to very low temperatures (or very high ice-supersaturations). Figure 2.6 shows the diagram of (2.95) with three different \( k \) values. All three curves are assumed to have a typical \( N_{IN} \) of 1 l\(^{-1}\) at -20°C in the atmosphere. One can observe that these curves tend to flatten out at about -40°C, which corresponds an ice supersaturation of 47.4%. Such a high supersaturation is quite unlikely to exist in natural clouds. So, it is safe to pick \( N_* \) at \( s_* = 0.474 \) (\( T_* = -40°C \)) as the upper limit for \( N_{IN} \). This would give a hypothetical total potential IN concentration, \( N_* \), of 11 l\(^{-1}\) for \( k = 3 \), 35 l\(^{-1}\) for \( k = 4.5 \), and 560 l\(^{-1}\) for \( k = 8 \) with the assumption of a typical \( N_{IN} \) of 1 l\(^{-1}\) at -20°C and water saturation.

As will be shown in the discussion of the diffusional growth of ice, ice crystals multiply their mass faster when they are smaller but vary in size faster when they are larger. Therefore, the initial shape of the ice crystals right after nucleation is not crucial to the overall growth. We may simply assume the nucleated ice crystals to be spherical or have an aspect ratio the same as the inherent growth ratio, which will be discussed in detail next. Because of the fast growth rate, the nucleated ice crystal will normally grow to 1 \( \mu \)m radius within a few seconds. We can thus assume that the initial ice is 1 \( \mu \)m in radius.
2.3.1.2. Freezing Nucleation

In contrast to the vapor-ice route considered in the previous discussion, the nucleation of ice can also proceed via the freezing of liquid. Due to the abundance of liquid drops, the freezing nucleation process is quite common in clouds, at least at low temperatures. There are several ways for a drop to freeze. As mentioned in Section 2.1, pure water freezes homogeneously at temperatures below about -40°C. Thus, homogeneous freezing may occur at or below -40°C, depending on the solute content in the drops. At higher temperatures, the freezing of a drop requires the assistance of foreign substances. *Immersion freezing* may occur when the drop contains ice nucleating substances, while *contact freezing* is possible when the drops come into external contact with ice-forming nuclei. Other means of triggering the crystallization of supercooled water have also been reported, such as the freezing induced by mechanical shocks, sonic...
shocks, and shock waves (Goyer et al., 1965; Foster and Pflaum, 1985), as well as the freezing of drops by collision (Czys, 1989) and through drop breakup (Koenig, 1965). In this study, we will only discuss the conventional freezing-nucleation process: the homogeneous freezing, immersion freezing, and contact freezing.

1. Homogeneous Freezing

Many laboratory studies and observation have shown that liquid drops exist at temperatures as low as -38°C, but not much below (Heymsfield and Sabin, 1989). Since there appear to be few effective ice nuclei in the upper troposphere, it is evident that ice nucleation may often take place by the homogeneous freezing of droplets. From the classical theory of nucleation, the homogeneous freezing rate can be expressed as (Pruppacher and Klett, 1980, p.178)

\[
J_{HF} = 2N_c \frac{\rho_w k T}{\rho_i h} \sqrt{\frac{\sigma_{wi}}{k T}} \exp\left(-\frac{\Delta F_{act} + \Delta G^*_{wi}}{k T}\right),
\]

(2.100)

where \(J_{HF}\) is the number of ice embryos reaching the critical radius per second per unit volume of water, \(N_c\) is the number of monomer molecules adjacent to a critical embryo, \(\rho_i\) is the ice density, \(\rho_w\) is the water density, \(T\) is temperature in K, \(k\) is Boltzmann's constant, \(h\) is Planck's constant, \(\Delta F_{act}\) is the activation energy for self-diffusion, and \(G^*\) is the critical energy above which the ice embryo will grow spontaneously and lead to the complete freezing of the droplet. This nucleation rate is basically a function of temperature, and can be parameterized from experimental data. Hagen et al. (1981) provided the formula

\[
J_{HF} = 5.92 \times 10^{38} T \cdot \exp\left(\frac{1.260 \times 10^5}{T} - 588.1\right),
\]

(2.101)

while the result by Demott and Rogers (1990) suggests
\[ J_{\text{HF}} = 7.94 \times 10^{10} \cdot \exp[-1.75(T - 239)] , \]  

(2.102)

where \( J_{\text{HF}} \) is in number \( \text{m}^{-3} \cdot \text{s}^{-1} \), and \( T \) is in K. The last equation is used in this study for its simplicity.

2. Heterogeneous (Immersion) Freezing

Experiments with the heterogeneous freezing of droplets containing impurities have shown that larger drops nucleate at higher temperature. Pruppacher and Klett (1980, pp. 274-277) pointed out that there are two types of theory for such phenomenon. The stochastic hypothesis explains the freezing behavior as a result of random fluctuations among water molecules to form ice germs, which is more effective in the presence of immersed foreign particles and with large volumes of water. The singular hypothesis attributes the heterogeneous freezing to the singular freezing characteristics of immersed AP. Larger drops will have more chance to contain AP that has higher characteristic nucleation temperature. The theoretical development for both hypotheses depends on the properties of the immersed AP, which is still unclear to date. Thus, we have to rely on experimental studies to get the nucleation rates for immerse freezing. Vali (1968) measured the nucleation rates of immersion freezing of drops made from rainwater and melted hailstones. His result was used by Danielsen et al. (1972) to derive the empirical formula

\[ n_i = \exp[-\gamma(7+T)] \quad T \leq -7 \degree\text{C}, \]

\[ n_i = 0 \quad T > -7 \degree\text{C}, \]  

(2.103)

where \( n_i \) is the number of nuclei per gram of water, \( \gamma = 0.68 \degree\text{K}^{-1} \), and \( T \) is in \degree\text{C}. Similar to the approach used for the heterogeneous deposition rate, we can take the derivative of the above equation against time:
\[
\frac{dn_i}{dt} = -\gamma \exp[-\gamma(7 + T)] \frac{dT}{dt}.
\]  \hspace{1cm} (2.104)

Therefore, for a drop of mass \(m_i\), the nucleation rate can be expressed as a function of the cooling rate:

\[
\frac{dN_i}{dt} = -m_i \gamma \exp[-\gamma(7 + T)] \frac{dT}{dt}.
\]  \hspace{1cm} (2.105)

### 3. Contact Nucleation

Ice particle concentrations in excess of conventionally measured ice nuclei have been observed frequently in slightly supercooled cumulus clouds (Keonig, 1963; Braham, 1964; Mossop et al., 1968) and orographic clouds (Hobbs, 1969; Auer et al., 1969). A number of processes might be responsible for the observed discrepancies, such as immersion freezing and secondary ice generation. Parungo (1973), Young (1974b), as well as Hobbs and Rangno (1985), suggested that contact nucleation might be the dominant primary ice generation mechanism at temperatures greater than -16°C. However, the study of Backer (1991) showed that the role of contact nucleation in the enhancement of ice nucleation is very small. Rangno and Hobbs (1991), as well as Chen and Lamb (1992b), suggest that the high ice concentrations at the relatively warm part of the mixed-phase clouds could be a product of heterogeneous deposition-nucleation that resulted from a high supersaturation in the air. Nevertheless, contact nucleation could still be important under certain conditions and is worthy of studying.

It is necessary to know the mechanisms by which water drops capture ice nuclei in order to calculate the rate of contact nucleation. The collection of ice nuclei by water drops can be achieved by hydrodynamic-inertial collision, turbulent diffusion, Brownian
diffusion, and phoretic forces. The Brownian collection kernel, given by Slinn and Hales (1971), is expressed as:

\[ K_{Br} = \frac{1}{n_p} \left. \frac{dN_p}{dt} \right|_{tBr} = 4 \pi r_w D_p f_p , \quad (2.106) \]

where \( n_p \) is the number concentration of particles in air, \( N_p \) is the number of contacts between particles and drops, \( r_w \) is radius of drop, \( D_p \) is diffusivity of small particle in air, and \( f_p \) is the ventilation coefficient for aerosol particles in air (see Appendix A for definitions). The expression for the thermophoretic transport was originally derived by Brock (1962):

\[ K_{th} = \frac{1}{n_p} \left. \frac{dN_p}{dt} \right|_{th} = 4 \pi r_w^2 f_h f_{th} \frac{Q}{P} , \quad (2.107) \]

where \( f_h \) is the ventilation coefficient of heat, \( f_{th} \) the empirical modification coefficient from Waldmann and Schmidt (1966), \( P \) is the air pressure, and \( Q \) is the heat flux (see Appendix A for definitions). Note that \( Q \) is proportional to the thermal conductivity of the particle, and is assumed to be that of water -- the major component of haze particles.

The diffusiophoresis collection kernel can be expressed as (Slinn and Hales, 1971):

\[ K_{df} = \frac{1}{n_p} \left. \frac{dN_p}{dt} \right|_{df} = 4 \pi r_w^2 f_v f_{df} \sqrt{\frac{M_w M_d}{\rho_a}} \frac{W}{\rho_a} , \quad (2.108) \]

where \( f_v \) is the ventilation coefficient of water vapor, \( f_{df} \) is the empirical modification coefficient = 0.85 to 1.0, \( M_w \) is the molecular weight of water, \( M_d \) is the molecular weight of dry air, \( \rho_a \) is the density of air, and \( W \) is the mass flux (see Appendix A for definitions).

Goldsmith and May (1966) find good experimental verification by using \( f_{df} = 1 \). By assuming the growth of the drop to be in steady state (drop at its wet bulb temperature), we have
\[ \kappa_a f_h (T_w - T_a) = L_v D_v f_v (\rho_{v,\infty} - \rho_s) = l_v D_v f_v (\rho_{v,\infty} - \rho_s) / M_w \]  \hspace{1cm} (2.109)

from which a simple relationship between the two phoretic collection kernels can be derived as follow:

\[ \frac{K_{df}}{K_{th}} = -\frac{M_w f_{df} R T}{M_d f_{th} l_v} \] \hspace{1cm} (2.110)

Figure 2.7 shows the possible values of this ratio as a function of the particle size and thermal conductivity. These two phoretic forces are generally opposite in sign, and diffusiophoretic force is normally smaller in magnitude than the thermophoretic force.

Figure 2.7: Variation of \( K_{df} / K_{th} \) as a function of particle radius and thermal conductivity at \( T = -10 \, ^{\circ}C \) and \( P = 500 \, \text{mb} \).
The experiment of Goldsmith and May (1966) and the theoretical consideration of Annis and Mason (1975) show that the two phoretic effects are not coupled and, therefore, the two phoretic kernels are additive. It is questionable, however, that this is true between Brownian diffusion and phoretic forces. For detailed hydrodynamic flow calculation, the overall collection kernel for a particle to move around a drop should be derived from the original equation of motions. Nevertheless, the direct summation of individual kernels
\[ K \cong K_{\text{Br}} + K_{\text{th}} + K_{\text{df}} + \ldots \]  (2.111)
can still be used as a low-order parameterization of the total collection since there are greater uncertainties in the distribution and physical properties of the aerosol particles.

Young (1974b) and Parungo et al. (1976) suggested that very small particles \((r < 40 \text{ nm})\) are desirable to promote contact with cloud droplets. But Dennis (1980, pp. 115-116) rejected their suggestion, based on AgI cloud seeding experimental evidences (Edwards and Evans, 1961; Sax and Goldsmith, 1972), that small particles were almost totally ineffective at temperatures down to -12°C. This is in accordance with Georgii and Kleinjung’s (1967) observation that large AP are effective IN, as mentioned in Section 2.3.1. We can therefore assume that AP smaller than 0.1 \(\mu\text{m}\) are not effective IN. Our attention can be limited to AP larger than 0.1 \(\mu\text{m}\). Although the effectiveness of large AP as ice forming nuclei is not strongly size dependent, it is important to remember that the size of AP does affect the collection rate. Yet, since there is not enough information about the size and composition distribution of natural AP, a 0.5 \(\mu\text{m}\) monodisperse AP population is thus applied in this study.

The number concentration of contact nuclei in natural air \((n_p)\) is difficult to determine. Young (1974b) deduced a value of 230 per liter at -4°C from Blanchard’s (1957) experimental data, which is within the range of large AP concentrations as
mentioned in Section 2.3.1. The temperature dependence of the contact nucleation ability of atmospheric aerosols is not well known. Therefore, all the large AP that serve as potential IN are assumed to act as contact nuclei as well. The total IN concentration, $N_\ast$, is set to be around 230 per liter near the surface in this study.

4. Freezing Time

The overall freezing of supercooled drops during the nucleation processes mentioned above can be described in three stages. During the initial stage, a portion of the liquid water solidifies and releases latent heat, which raises the drop temperature to near 0 °C. This process occurs in a very short period of time so that no appreciable heat is transferred to the ambient air, hence this step is termed the "adiabatic" stage of freezing. The amount of water that remains unfrozen can be derived according to the energy conservation requirement such that the total heat in the particle before freezing is the same as that after freezing:

$$H_o = m_o [\theta_w (T_o) + l_f (T_o)] = m_i \theta_i (T_o) + m_w [\theta_w (T_o) + l_f (T_o)] = m_w l_f (T_o) ,$$

(2.112)

which can be rearranged to get

$$m_w = m_o - m_i = m_o \left[ \frac{\theta_w (T_o) + l_f (T_o)}{l_f (T_o)} \right] ,$$

(2.113)

where $m_o$ is the initial drop mass, $m_w$ and $m_i$ are the masses of unfrozen and frozen water, $\theta_w$ and $\theta_i$ are the sensible heats of water and ice, $l_f$ the latent heat, and $T_\infty$ is the initial drop temperature, which is assumed to be the same as the air temperature.

Since the temperature of the partially frozen drop is warmer than the ambient air, heat may be lost due to conduction to the air and through evaporation of water. The subsequent stage of freezing is a relatively slower, heat transfer limited freezing process
with a freezing rate determined by the differences of temperatures and saturation ratios between the drop and the air. The amount of time required for a drop to freeze completely can be determined by analyzing the mass and heat transfer equations,

\[
\frac{dm_w}{dt} = 4\pi r \frac{D_v f_v}{R_v} \left( \frac{e_\infty}{T_\infty} - \frac{e_{sw}(T_o)}{T_o} \right) \equiv \alpha f_v \frac{\Delta t}{r},
\]

(2.114)

\[
\frac{dH}{dt} = 4\pi r \left( \kappa_h f_h (T_\infty - T_o) + \frac{dm_w}{dt} \right) h_v (T_o) \equiv r (\beta_1 f_h + \beta_2 f_v),
\]

(2.115)

where

\[
\alpha = 4\pi \frac{D_v}{R_v} \left( \frac{e_\infty}{T_\infty} - \frac{e_{sw}(T_o)}{T_o} \right), \quad \beta_1 = 4\pi \kappa_h (T_\infty - T_o), \quad \text{and} \quad \beta_2 = \alpha h_v (T_o)
\]

are functions of \(T_\infty\) and \(e_\infty\) only. As will be justified later, the size of the drop does not change much during the freezing process, which permits us to assume that ventilation coefficients \(f_h\) and \(f_v\) remains constant. At the time \(t = \Delta t\) when all the liquid has just become frozen, the temperature of the new ice particle is \(T_o = 0\) °C and its total heat \(H_1\) can be expressed as

\[
H_1 = m_0 \vartheta(T_o) = 0 = H_o + \int_{0}^{\Delta t} \frac{dH}{dt} dt = H_o + (\beta_1 f_h + \beta_2 f_v) \int_{0}^{\Delta t} r dr.
\]

(2.116)

Applying \(m_w = \frac{4}{3} \pi r^3 \rho_w\), we can rewrite (2.114) as

\[
\frac{dm_w}{dt} = 4\pi \rho_w r^2 dr = \alpha f_v \frac{\Delta t}{r} dt,
\]

(2.117)

which can be used to replace the integrand in (2.116)

\[
\frac{dt}{\alpha f_v} = \frac{1}{r} \frac{dr}{r}.
\]

(2.118)

Thus, (2.116) is transformed into

\[
\int_{0}^{\Delta t} r dr = \frac{1}{\alpha} \int_{0}^{\Delta t} r^2 dr = \frac{-H_o}{(\beta_1 f_h + \beta_2 f_v)} \equiv \gamma,
\]

(2.119)
where \( r_o \) is the initial drop size and, from (2.118),
\[
    r_i = \sqrt{r_o^2 - 2\alpha \Delta t}\tag{2.120}
\]
is the drop size at \( t = \Delta t \). We thus obtain, from (2.119) and (2.118), the analytical solution for \( \Delta t \):
\[
    \Delta t = \frac{(3\alpha \gamma + r_o^3)^{2/3} - r_o^2}{2\alpha}.
\tag{2.121}
\]

Figure 2.8 is a plot of \( \Delta t \) as a function of air temperature (degree of supercooling) and drop size in a water-saturated environment where \( e_\infty = e_{s,w}(T_\infty) \). Note that the freezing time at \( T_\infty \) near 0°C is large because the rate of conduction is small when \( (T_o - T_\infty) \) is small. From (2.118), we can see that \( \Delta t \) is proportional to \( r^2 \) and \( 1/\alpha' \). Let us simplify \( \alpha' \) by utilizing the Clausius-Clapeyron equation:
\[
    \frac{e_\infty - e_{s,w}(T_o)}{T_o - T_\infty} = \frac{e_{s,w}(T_o)}{T_o} \left[\frac{T_o}{T_\infty} \exp\left(\frac{L_f}{R_v} \frac{T_o - T_\infty}{T_o T_\infty}\right) - 1\right]. \tag{2.122}
\]
Consider temperatures not too much lower than \( T_o \) and apply the first-order approximation of \( \exp(x) \approx 1 + x \), so \( \alpha' \) can be simplified as
\[
    \alpha = \frac{D_v f_v e_{s,w}(T_o)}{\rho_w R_v T_o} \left[\frac{T_o}{T_\infty} \exp\left(\frac{L_f}{R_v} \frac{T_o - T_\infty}{T_o T_\infty}\right) - 1\right] \approx \frac{D_v f_v e_{s,w}(T_o)}{\rho_w R_v T_o T_\infty} \left(\frac{L_f}{R_v T_\infty} + 1\right)(T_o - T_\infty), \tag{2.123}
\]
which is roughly proportional to the supercooling \( (T_o - T_\infty) \). Here, we have ignored the curvature and solute effects on \( e_{s,w} \). Using the equations derived above, it can be shown that the change of drop size during freezing is less than 2% under normal atmospheric conditions so that the assumption of constant \( f_h \) and \( f_v \) can be justified.
Figure 2.8: Time required for droplets to freeze completely after nucleation as a function of the degree of supercooling and drop size.

The role of evaporation in determining the freezing time $\Delta t$ can be shown by ignoring the evaporation term $\frac{dm_w}{dt}$ in (2.114) and (2.115). The freezing time without the effect of evaporation-cooling is expressed as

$$
\Delta t' = \frac{-H_o}{\beta_1 f_h r_o}.
$$

(2.124)

Compare $\Delta t$ with $\Delta t'$, one can find that

$$
\frac{\Delta t}{\Delta t'} = 1 + \frac{\beta_2 f_v}{\beta_1 f_h}.
$$

(2.125)

The mass ventilation coefficient of water vapor and the ventilation coefficient of heat in the air for a drop are very similar in value, and can be assumed to be the same for our purposes. So, the ratio of the two freezing times can be expanded into

$$
\frac{\Delta t}{\Delta t'} \approx 1 + \frac{\beta_2}{\beta_1} = 1 + \frac{k_{\infty}(T_o - T_e)}{D_v \left[ e_{\infty} - e_{s,w}(T_o) \right]}.
$$

(2.126)
Applying the Clausius-Clapeyron equation and its first-order approximation, we get

\[
\frac{\Delta t}{\Delta t'} \approx 1 + \frac{R_v \kappa_w T_o T_o}{D_v e_{sw}(T_o) \left[ \frac{L_f}{R_v T_o} - 1 \right]}.
\]  

(2.127)

This ratio is independent of drop radius since we assumed \( f_v = f_h \). With a supercooling of 10°C, the freezing time with evaporation is 63% of that without evaporation. As the supercooling increases, the conduction term becomes more important, and the value becomes 70%, 76%, and 81% for a supercooling of 20, 30, and 40°C, respectively.

After complete freezing, the transfer of heat and water vapor from the particle to the air will continue. In this last stage, there is no more latent heat available to maintain the particle temperature at 0°C. Now, conduction and evaporation will gradually bring the particle's temperature close to that of the ambient air.

5. **Stiffness of the Freezing Equation**

As shown in Figure 2.8, the time scale for the freezing process varies over several orders of magnitude. Instead of finding a numerical scheme to solve the problem of stiffness, we can make the assumption that the first two stages of the freezing process are always completed within one typical time step based on two reasons. First, the freezing time is larger than the typical time-step (1 second) only when the drop size is very large or the air temperature is near 0°C. But large drops are rare in the cloud and the assumption of instantaneous freezing will not affect the overall microphysics by much, and the freezing process is not important at high temperatures. Second, a few seconds of error in the freezing time is quite trivial compared with the uncertainties in the ice nucleation theory. So, to further the approximation, we may even ignore the third stage and assume the frozen particles reach equilibrium in temperature with the air very quickly.
2.3.2. Diffusional Growth of Ice Particles

The saturation vapor density over ice is less than that over liquid water at the same temperature. Thus, water vapor tends to deposit preferentially onto the surfaces of ice particles when both phases are present. Due to the relatively low concentrations of IN, this so called Bergeron-Findeison process is an important mechanism in forming large precipitable particles when the growth of droplets is not effective. Except in the tropics, the depositional growth of ice crystal is often crucial to the initiation of precipitation.

2.3.2.1. Linear Growth Rate

The depositional growth of ice crystals is more complicated than that of droplets, partly because of their nonspherical shapes. Simple ice crystals have the general form of hexagonal prisms, with two basal faces and six prism faces. Two distinct sets of axes may generally be identified, namely, the $c$ (principal) axis perpendicular to basal faces and the $a$ (lateral) axes that point to the edges joining adjacent prism faces. A plate-like crystal is formed if water vapor deposits mainly on the prism faces (extending the $a$ axis), and columnar ice is formed if the growth is mainly on the basal faces. The preferential growth of ice along either axis set is dictated largely by temperature (Kobayashi, 1961) and defines these primary growth habits. However, the $c$-to-$a$ ratio (or the aspect ratio) of an ice crystal does not stay constant during growth but varies according to the ambient temperature and the ambient supersaturation. Ice crystals may grow into even more complicated structures, such as dendritic or skeletal shapes. All such variations of form from the primary habits are called secondary habits.
1. Laboratory Experiments and Observations of the Linear Growth Rates

The habits of ice crystals exhibit very strong dependence on temperature and, to a lesser degree, on supersaturation (Nakaya, 1954; Hallet and Mason, 1958; Kobayashi, 1961). Many workers have noted the transitions of the primary habits from plate to column (~ -4°C), back to plates (~ -9°C) and then to column again (~ -22°C) as the temperature decreases (Kobayashi, 1961; Hallet and Mason, 1958; Fukuta, 1969; Ryan et al., 1976). This remarkable temperature dependence of the primary growth habits gives evidence for the fundamental difference of the linear growth rates of individual basal and prism faces. The direct measurements of the linear growth rates of individual prism and basal faces of ice grown on a substrate were made as functions of temperature (-2.5 to -17°C), excess vapor pressure, and partial pressure of air by Lamb and Scott (1972). They measured the linear growth rates in a pure water vapor environment to eliminate the effect of air on the transport of water vapor to the crystal surfaces. Lamb and Scott (1974) attributed the variation of the growth rates with temperature to the peculiar trends in the condensation coefficients and the effect of crystal surface kinetics. Sei and Gonda (1989) measured the condensation coefficients from 0 to -30°C and adopted the so-called vapor/liquid/solid growth mechanism proposed by Kuroda and Lacmann (1982) to interpret the habits of ice crystals growing at temperatures near the melting point.

While the primary habits are strongly correlated with temperature, the secondary habits are controlled largely by the supersaturation or the growth rate. In their laboratory measurements of ice crystals growing in air, Shaw and Mason (1955) were able to give a crude description of the growth of the faces:

\[
(2a)^2 = U_a t + A , \tag{2.128}
\]

\[
(2c)^2 = U_c t + B .
\]
where $U_a$, $U_c$, A, and B are constant, and $t$ is the time of growth. Todd (1965) measured the sizes of crystals along the $c$ and $a$ axes, sampled in cumulus clouds and found deviations from the $t^{1/2}$ law. He proposed that $U_a$, $U_c$, and the exponent of the power law should be temperature dependent. Ono (1969, 1970), Auer and Veal (1970), Heymsfield and Knollenberg (1972), Davis (1974), as well as Jayaweera and Ohtake (1974) measured the dimensions of naturally occurring ice crystals and found an exponential relationship between the two axes of the following form:
\[
c = \alpha a^\beta,
\]
where $\alpha$ and $\beta$ are positive constants and have specific values corresponding to the particular crystal types.

2. Historical Review of the Simulations of the Linear Growth Rates

Hall and Pruppacher (1976) adopted the exponential relationship (2.129) to describe the characteristic dimensions of the $c$ and $a$ axes. However, since only one set of coefficients is used to represent either columnar or planar ice, their results overlooked the temperature dependence of the secondary habits. Miller and Young (1979) suggested the existence of three principal stages of ice crystal growth from the vapor: (1) isometric growth, (2) constant axial ratio growth, and (3) limiting dimension growth. Very small ice crystals ($< 3 \, \mu m$) grow nearly isometrically, that is, uniaxially. The crystals then enter a stage where they attain a characteristic axis ratio. Large crystals grow mainly along the major axis and the dimension of the minor axis is limited. Miller and Young assume that the minor axis will cease to grow after reaching a limiting dimension. Their constant axial ratio and the limiting dimension are both temperature dependent and, therefore, reflect the secondary habits to some extent. However, the artificial division of the growth into separate stages emulates a discrete process that does not exist in nature.
Also, neither the temperature-dependent surface kinetic nor the gas-phase kinetic effects can be properly described with such a scheme. Hindman and Johnson (1972) applied the expression developed by Todd (1965) for the growth along the $c$ and $a$ axes at a constant temperature in a water saturated environment:

$$a = K_a t^A,$$

$$c = K_c t^B,$$

(2.130)

where $K_a$, $K_c$, $A$, and $B$ are parameters which depend only on the temperature, and $t$ is the time of growth. Note that these two formulas can be combined to give

$$c = \alpha a^\beta,$$

(2.131)

with $\alpha = K_c / K_a^{A/B}$, and $\beta = B/A$. This expression is an improvement over (2.129) in that both $\alpha$ and $\beta$ are temperature dependent. The value of $\beta$ they used does reflect the transition of the primary habits at -4, -9, and near -20°C except that $\beta$ is set to unity at above -4 and below -20°C.

Equation (2.131), because of its coupling to (2.130), provides a better parameterization for the linear growth rates than the simple empirical representation (2.129) because of the inclusion of the temperature dependent coefficients, despite the fact that the values they used for $A$ and $B$ are oversimplified. The above formulas are derived according to experimental data but the physics behind it was not explained. In the following discussions, a more physically-based theoretical explanation will be provided for the growth habits.

### 3. Theoretical Discussion

Let us first examine the factors that differentiate the growth rates on the prism and basal faces. As suggested by Lamb and Scott (1974), the condensation coefficients along the $a$ axis ($\alpha_a$) and along the $c$ axis ($\alpha_c$) control the primary habits and determine the
characteristic growth. Another important factor that may contribute to the differential growth rates is the different vapor fluxes to the two faces due to the asymmetrical shape of the ice crystals. For stationary ice particles, the vapor flux is proportional to the vapor density gradient $\nabla \rho$. Thus, the linear growth rates have the following proportionality:

$$\frac{da}{dt} \propto \alpha_a(T) \nabla \rho_a, \quad (2.132)$$

$$\frac{dc}{dt} \propto \alpha_c(T) \nabla \rho_c. \quad (2.133)$$

The ratio between the two linear growth rates is then

$$\frac{dc}{da} = \frac{\alpha_c(T) \nabla \rho_c}{\alpha_a(T) \nabla \rho_a} \equiv \Gamma(T) \Phi(c,a), \quad (2.134)$$

where $\Gamma(T) \equiv \alpha_c(T) / \alpha_a(T)$ and $\Phi(c,a) \equiv \nabla \rho_c / \nabla \rho_a$. We call the ratio of the two condensation coefficients, $\Gamma$, the \textit{inherent growth ratio}, a function of temperature alone. The parameter $\Phi$ is a function of the dimensions $a$ and $c$ of the ice crystals and can be derived by solving Laplace’s equation for diffusion problems.

The distribution of water vapor density $\rho$ in the region surrounding an ice crystal growing under quasi-steady state conditions satisfies Laplace's equation $\nabla^2 \rho = 0$. The solution of this equation, with the boundary condition $\rho = \rho_s$ on the particle surface and $\rho = \rho_\infty$ at infinity (ambient air), is the same as that for the diffusion growth of water drops:

$$\rho = \rho_\infty - \Delta \rho \frac{a}{r}, \quad (2.135)$$

where $\rho$ is the water vapor density at a distance $r$ from the center of the sphere, $\Delta \rho = \rho_\infty - \rho_s$, and $a$ is the radius of the sphere. However, the nonspherical shape of an ice crystal introduces complicated boundary conditions which impose great difficulty in solving the Laplace equation. We need to idealize the geometry of the ice crystals.
Jayaweera and Cottis (1969) have shown that spheroids are good analogs for simple columnar and plate-like ice crystals. As shown in Figure 2.9, oblate spheroids resemble plate-like ice crystals, and prolate spheroids resemble columnar ice. To solve the Laplace Equation with spheroidal boundary conditions, it is convenient to use spheroidal coordinates instead of the spherical coordinates that were used in deriving (2.135). Since the spheroids are symmetric about the $c$ axis, we can reduce the dimensions along the $c$ and $a$ axes to an elliptical coordinate system $(\mu, \theta)$, as shown in Figure 2.10. To change from elliptical coordinates to the Cartesian coordinates $(x,y)$, corresponding to the $a$ and $c$ directions, respectively, we use the following conversion:

$$\mu = \frac{r_1 + r_2}{2},$$

(2.136)

where $r_1 = \sqrt{(x+d)^2 + y^2}$ and $r_2 = \sqrt{(x-d)^2 + y^2}$. Therefore, in elliptical coordinates, the constant-$\rho$ contours lie on constant-$\mu$ surfaces as shown in Figure 2.10. The solution of Laplace’s equation, with boundary conditions of $\rho = \rho_\infty$ at $\mu = \infty$ and $\rho = \rho_s$ at $\mu = \mu_o$, can now be obtained in a form similar to (2.135):

$$\rho = \rho_\infty - \Delta \rho \frac{\mu_o}{\mu}.$$  

(2.137)

The vapor density gradient is thus

$$\frac{\partial \rho}{\partial \mu} = \Delta \rho \frac{\mu_o}{\mu^2},$$

(2.138)

or in Cartesian coordinates

$$\frac{\partial \rho}{\partial x} = \frac{\partial \rho}{\partial \mu} \frac{\partial \mu}{\partial x}, \quad \frac{\partial \rho}{\partial y} = \frac{\partial \rho}{\partial \mu} \frac{\partial \mu}{\partial y}. \quad \text{(2.139)}$$

Combining (2.136), (2.137), and (2.139), the ratio between the vapor density gradients over the basal faces $(x=0, y=c)$ to that over the prism faces $(x=a, y=0)$ is found to be
Figure 2.9: Perspective views of prolate and oblate spheroids that resemble columnar and planar ice crystals, respectively.

Figure 2.10: Elliptical coordinate (\(\mu, \theta\)) and the constant \(\mu\) surfaces. The shaded area represents the spheroidal approximation of an ice particle while the constant \(\mu\) contours represent constant vapor density isopleths around the ice crystals.
\[ \Phi \equiv \frac{\nabla \rho(0,c)}{\nabla \rho(a,0)} = \frac{\left( \frac{\partial \rho}{\partial \gamma} \right)_{x=0,y=c}}{\left( \frac{\partial \rho}{\partial \alpha} \right)_{x=a,y=0}} = \frac{c}{a}, \quad (2.140) \]

which is simply the aspect ratio \( \phi \equiv \frac{c}{a} \). Now, the ratio of the linear growth rates can be expressed simply as

\[ \frac{dc}{da} = \Gamma(T) \phi. \quad (2.141) \]

By comparing this result with the derivative of the empirical relationship (2.131),

\[ \frac{dc}{da} = \beta \alpha a^\beta / a = \beta \left( \frac{c}{a} \right) = \beta \phi, \quad (2.142) \]

one may notice the resemblance between the theoretical result and that from observations. The differential forms of both formulae exhibit a direct proportionality between the ratio of the linear growth rates and the aspect ratio \( \phi \). Also, since \( \beta \) depends on the crystal types which, in turn, depend on temperature, one can readily identify \( \beta \) to with the temperature-dependent growth habit ratio \( \Gamma \). In fact, the values of \( \beta \) from observational result correspond remarkably well with the experimental values of \( \Gamma \). The composite Figure 2.11 compares the parameter \( \beta \) from observational data with the parameter \( \Gamma \) from experimental data. The thick line indicates data from Lamb and Scott (1972) while the dotted-line is from Sei and Gonda (1989). The shaded circles represent the values from observational data. We can see a fairly good correlation. It is thus suggested here that the empirical parameter \( \beta \) is a direct reflection of the inherent growth ratio \( \Gamma(T) \), and is thus controlled by fundamental surface-kinetic processes. The thin line in Figure 2.11 represents a summary of the available information, which is constructed as the inherent growth ratio used in this study.
Figure 2.11: Comparisons between the experimental and observational data for the inherent growth ratio. The thick line is from Lamb and Scott (1972); dotted line is from Sei and Gonda (1989) with actual data points denoted as black squares. The shaded ellipses 1 to 8 are from Ono (1970), 9 to 14 from Auer and Veal (1970), 15 from Heymsfield and Knollenberg (1972), and 16 from Jayaweera and Ohtake (1974).
4. Ventilation Effect

The empirical expression (2.129) fits the observational data quite well except for particles of several hundred micrometers and larger in size. Figure 2.12 shows the typical relationship between the lengths of the \( a \) and \( c \) axes of observed ice crystals (c.f. Figure 20 in Ono, 1970). A perfect power-law relationship is followed until the long axis reaches several hundred micrometers. Such deviation can be explained by the ventilation effect on the diffusional growth. Recall that the ratio of the vapor fluxes for stationary ice crystal is proportional to the ratio of the vapor density gradients: \( \Phi(c,a) = \nabla \rho_c / \nabla \rho_a \). However, as ice particles fall through the air, the effect of ventilation enhances the vapor flux, especially on the long axis. If we let the ventilation effect on the vapor flux be \( f \), equation (2.141) can be modified as follows:

\[
\frac{dc}{da} = \Gamma(T) \phi(c,a) = \Gamma(T) f \phi ,
\]

(2.143)

Figure 2.12: Schematic diagram of the observed ice crystal axial ratio relationship.
where \( f \) is a function of \( a \), \( c \) and the properties of air. Thus, the relationship between \( a \) and \( c \) with the ventilation effect can be expressed as

\[
c = \alpha a^{\Gamma^*},
\]

(2.144)

where \( \Gamma^* = \Gamma(T)f \). The ratio \( f \) of the local ventilation factor for the \( a \) and \( c \) axes is not well known. However, we can derive a first-order approximation for \( f \) from existing data. Hall and Pruppacher (1976) compiled data from Pitter et al. (1974) and other sources to obtain empirical formulas for the overall (average) ventilation effect for the whole particle:

\[
\bar{f} = \alpha + \beta X^\gamma,
\]

(2.145)

with \( X = N_\text{Sc}^{1/3} N_\text{Re}^{1/2} \), and

\[
\begin{align*}
\alpha &= 1.0, \quad \beta = 0.14, \quad \gamma = 2 \quad \text{for } X \leq 1, \\
\alpha &= 0.86, \quad \beta = 0.28, \quad \gamma = 1 \quad \text{for } X > 1,
\end{align*}
\]

where \( N_\text{Sc} \) is the Schmidt number and \( N_\text{Re} \) is the Reynolds number of the spheroidal particle. Such formulae are based on the expression given by Mason (1971), which actually applies to \( X \leq 1 \):

\[
\bar{f} = 1 + \left( \frac{V r}{2\pi D_v} \right)^{1/2}.
\]

(2.146)

Here, \( V \) is the fall velocity, \( r \) is the radius of a spherical particle, and \( D_v \) the diffusivity of water vapor in air. We can see from the above equation that Reynolds number is proportional to \( r \) for a fixed \( V \). Pitter et al. (1974) also indicated that \( N_\text{Re} \) is proportional to the characteristic length of the particle. To a first approximation, one may assume that the ventilation effect is inversely proportional to the curvature at a specific location on the particle surface. The local ventilation coefficients can be related to \( \bar{f} \) by comparing the local curvature with \( 1/r_o \), where \( r_o \) is the radius of a spherical particle that has the same \( \bar{f} \).
One can use the spherical equivalent radius or the capacitance $C$ of the ice particle for $r_0$. The local ventilation coefficients at the $c$ and $a$-axes are therefore approximated as:

$$
f_c \approx \alpha + \beta X^{\gamma} \left( \frac{c}{r_0} \right)^{\gamma/2},
$$

$$
f_a \approx \alpha + \beta X^{\gamma} \left( \frac{a}{r_0} \right)^{\gamma/2}.
$$

(2.147)

For all practical purposes, we can use $\gamma = 1$ in the exponent of the ratio of curvatures since the ventilation effect is only important when $X > 1$. The parameter $f$ can thus be written as

$$
f = \frac{f_c}{f_a} \approx \frac{\alpha + \beta X^{\gamma} \left( \frac{c}{r_0} \right)^{1/2}}{\alpha + \beta X^{\gamma} \left( \frac{a}{r_0} \right)^{1/2}}.
$$

(2.148)

Figure 2.13 shows $f$ as a function of the aspect ratio and the spherical equivalent radius of the ice particles. The value of $f$ is near unity for particles that are either small in size or have an aspect ratio near unity. For large ice particles, $f$ approaches the square root of the aspect ratio. Applying the ratio $f$ to equations (2.142) or (2.143), we are able to reconstruct the observed relationship (Figure 2.12) between the of $c$- and $a$-axes length, as shown in Figure 2.14. The particles are initially spherical with 1 $\mu$m radius and are assumed to grow with certain inherent growth habits $\Gamma$. The relationship between $c$- and $a$-axes is initially log-linear, but it gradually deviates from this dependence as the sizes become large and local ventilation effects become important. Figure 2.14 shows great similarity to the observational results in Figure 20 of Ono (1970).
Figure 2.13: The ratio of local ventilation coefficients for the \( c \) axis to that at the \( a \) axis as a function of the aspect ratio and equivalent radius of the ice particles.

Figure 2.14: The calculated lengths of \( c \) and \( a \) axes of ice particles grown at various values of the inherent growth habit \( \Gamma \).
5. Change of Aspect Ratio

Equation (2.142) describes the observed linear growth rates from a theoretical approach. Together with the mass growth equation that will be introduced in the next section, we are able to derive a complete description of the depositional growth of ice. However, it is convenient to convert the linear growth rates into the change of aspect ratio by taking the logarithmic derivative of the volume of a spheroid, \( V = \frac{4}{3} \pi a^3 \phi \):

\[
\frac{d \ln V}{d \ln a} = 3 + \frac{d \ln \phi}{d \ln a}.
\] (2.149)

The derivative of \( \phi = \frac{c}{a} \) can be expanded into

\[
\frac{d \phi}{d a} = \frac{1}{a} \frac{dc}{da} - \frac{c}{a^2} \frac{da}{d a} = (\frac{dc}{da} - \phi) \frac{d \ln a}{d \ln a}.
\] (2.150)

Now, by replacing \( \frac{dc}{da} \) with (2.141) and combining the last two equations, we derive the expression for the change of aspect ratio as a function of the volume change:

\[
\frac{d \ln \phi}{d \ln V} = \frac{\Gamma - 1}{\Gamma + 2}.
\] (2.151)

The parameter \( \Gamma \) determines the direction of change of \( \phi \). For example, in the temperature regime where \( \Gamma > 1 \) (columns), the shape of ice crystal will become more (less) columnar during growth (decay) regardless of its original shape. This means that whereas the change of the primary habits is controlled by temperature, the magnitude of the change of \( \phi \), on the other hand, is determined by both \( \Gamma \) and the volume change. To consider the ventilation effect, one only has to replace \( \Gamma \) with \( \Gamma^* \). The change of volume can be derived from the mass growth rate and the deposition density, which is discussed next.
2.3.2.2. Mass Growth Rate

The diffusional mass growth of an ice particle follows very closely with that for drop growth. Applying the electrostatic analogy in spheroidal coordinates, the mass flux over the surface \( A \) of the ice particle is given by

\[
\frac{dm}{dt} = \int_A D \nabla \rho \cdot \hat{n} \, dA = 4 \pi C D \Delta \rho, \tag{2.152}
\]

where \( C \) is the electrostatic capacitance of the particle. For oblate spheroids, the capacitance is given by

\[
C = \frac{a \varepsilon}{\sin^{-1} \varepsilon} = \frac{d}{\sin^{-1} \varepsilon}, \tag{2.153}
\]

where the eccentricity \( \varepsilon = \sqrt{1-c^2/a^2} = \sqrt{1-\phi^2} \) and the length of foci \( d = \sqrt{a^2-c^2} = a \varepsilon \). For prolate spheroids,

\[
C = \frac{c \varepsilon}{\ln[(1+\varepsilon) \phi]} = \frac{d}{\ln[(1+\varepsilon) \phi]}, \tag{2.154}
\]

where \( \varepsilon = \sqrt{1-a^2/c^2} = \sqrt{1-\phi^{-2}} \) and \( d = \sqrt{c^2-a^2} = c \varepsilon \). When \( d = 0 \), the particle is spherical and \( C \) reduces to the radius \( r \) of the particle. Detailed derivations of (2.153) and (2.154) can be found in Snow (1954; p. 9, pp. 55-57). Measurements by McDonald (1963) of the capacitances of metal models of snow crystals agree very well with the above theoretical values for the idealized geometries.

1. Deposition Density

The linear growth rate equation, together with the mass growth equation, can only describe the evolution of the primary habits of ice crystals, but nothing about the various secondary growth habits. Magono and Lee (1966) attempted to bring order into the diversity of crystal shapes through their 80-category classification, which is a
simplification of nature, but still too complicated for this numerical study. There is one observable and well-documented parameter, however, that can be used as an approximation for the secondary habits: the deposition density.

The crystal density is defined as the crystal mass divided by the apparent volume that circumscribes the maximum $a$ and $c$ axis-extensions of the crystal. Crystals with branching or regions of incompleteness, such as dendrites or hollow columns, have lower densities than solid ice. The crystal densities provide extra information that adds to the primary habits and can be regard as a first-order approximation to the secondary habits. Fukuta (1969) measured the deposition density of ice crystals as functions of temperature and supersaturation, which is adopted for this study. We can thus calculate the change of the apparent volume due to depositional growth from the mass growth equation and the deposition density.

2. Heat Transfer Equation

To complete the description of the diffusional growth process, we also need to know the heat transfer equation:

$$\frac{dH_i}{dt} = \left( \frac{dH_i}{dt} \right)_{\text{cond}} + \left( \frac{dH_i}{dt} \right)_{\text{diff}},$$

(2.155)

with the two right-hand-side terms, the total heat from the air by conduction and from water vapor, given as

$$\left( \frac{dH_i}{dt} \right)_{\text{cond}} = 4\pi C_k \delta \left( T_\infty - T_i \right)$$

and

$$\left( \frac{dH_i}{dt} \right)_{\text{diff}} = h_v \left( \frac{dm_i}{dt} \right)_{\text{diff}},$$

(2.156)

where $H_i$, $m_i$ and $T_i$ are the total heat, mass and surface temperature, respectively, of the ice particle, $C_k$ is the heat conductivity of air, $h_v$ is the specific total heat of water vapor. Note that the electrostatic analogy also applies to the heat conduction equation.
3. **Modification factors**

Equations (2.152) and (2.155) describe the diffusional growth of ice crystals in an idealized situation. In more realistic situations, the modification factors that are used for the diffusional growth of droplet, as mentioned in Section 2.2.2, should also be applied. The modified mass growth equation is then

\[
\frac{dm}{dt} = 4 \pi C D_v \Delta \rho f_v f_{\text{kin}} f_{\text{prx}},
\]

(2.157)

where \( f_v, f_{\text{kin}}, \) and \( f_{\text{prx}} \) account for the mass ventilation, surface-kinetic, and proximity effects, respectively. Similarly, the modified conduction heating equation is

\[
\left. \frac{dH_i}{dt} \right|_{\text{cond}} = 4 \pi C k_v (T_\infty - T_i) f_h f_{\text{kin}}^* f_{\text{prx}}^*,
\]

(2.158)

where \( f_h, f_{\text{kin}}^*, \) and \( f_{\text{prx}}^* \) are the ventilation, surface-kinetic, and the proximity effects of heat. The ventilation and gas kinetic effects are similar to those for drop growth.

The source and sink proximity effect for ice crystal is somewhat different from that for droplets. In a mixed-phase environment where the drop concentration is usually much higher than that of the ice crystals, the proximity effect for an ice crystal is usually from water drops. Ice crystals can influence each other only when their concentration is very high. Marshall and Langleben (1954) considered a single ice crystal growing in a liquid drop environment and concluded that the growth rate of an ice crystal is enhanced by a factor

\[
f_{\text{prx}} = 1 + \left( 4 \pi \sum r_w \right)^{1/2} C,
\]

(2.159)

where the radius summation is over all the drops in 1 cm\(^3\) while \( r_w \) and \( C \) are in cm. The corresponding \( f_{\text{prx}}^* \) for the heat equation is the same as \( f_{\text{prx}} \) (Miller and Young, 1979).
2.3.3. Hydrodynamic Interactions

The processes of ice particles collecting droplets and other ice particles are called *accretion* and *aggregation*, respectively. These hydrodynamic interactions can be described by the same scalar transport equation used for the drop interactions, but with different collection efficiencies. Due to the complicated shapes of snow crystal, the superposition method used in determining the collection efficiencies for drop-drop interactions has proven to be the only feasible means for describing the ice-phase interactions (Pruppacher and Klett, 1980, p. 495). The available studies on collision efficiencies between ice crystals and drops were done mostly through such theoretical approach with limited observational measurements for verification. Detailed discussion of the collision efficiencies will be presented in Section 3.5.4. The coalescence efficiency for droplets in contact with ice particles is assumed to be unity.

The density of the rime-ice was first measured in the laboratory by Macklin (1962), who provided an empirical formula in the form of:

\[
\rho = f \left( -\frac{V_{imp} r}{T_s} \right) \equiv f(-A) = 0.11 \left( -\frac{V_{imp} r}{T_s} \right)^{0.76},
\]

(2.160)

where \(\rho\) is in g cm\(^{-3}\), \(r\) the radius of the collected drop, \(T_s\) the temperature of the ice substrate in °C, and \(V_{imp}\) the impact velocity of the drop. Empirical formulae for the impact velocity can be found in Rasmussen and Heymsfield (1985). Heymsfield and Pflaum (1985) modified Macklin's equation as:

\[
\rho = 0.30A^{0.44}, \quad \text{for } T \leq -5^\circ \text{C or } A \leq -1.6
\]

\[
= \exp(-0.03115 - 1.7030A + 0.9116A^2 - 0.1224A^3), \text{otherwise.}
\]

(2.161)
Note that Rasmussen and Heymsfield (1985) mistakenly gave the condition for using the upper formula as $A \geq -1.60$.

The aggregation of ice particles is not included in this study for two reasons. First, the efficiency of two ice particles sticking together is poorly known, especially for branched ice particles. Second, there is no simple way to approximate the aspect ratio and the apparent density of the aggregated ice, which are essential for the multi-component particle framework used in the study.

1. Aspect Ratio of Rimed Ice Particles

The assumption of a spheroidal shape is still maintained for ice particles that grow by riming. Normally, the rime-ice is collected on the face pointing into the air flow. It is, therefore, assumed that plannar ice particles grow on their $c$-axis while columns grow on the $a$-axis during riming. A schematic diagram of the change of aspect ratio due to riming is shown in Figure 2.15. The long axis for either columnar or plannar ice crystals remains unchanged, except when the collected drop is larger than the ice crystal. Thus, the new $a$-axis length for plates (oblate spheroids) can be expressed as:

$$a_{new} = \max(a, r), \quad (2.162)$$

where $a$ is the old $a$-axis length and $r$ is the largest collected drop radius. The volume of the newly collected rime-ice, $V_{\text{rime}}$ can be obtained from the accreted mass and rime density. So, the new volume of the ice particle $V_{new} = V + V_{\text{rime}}$, where $V$ is the original volume. According to the formula for the volume of a spheroid

$$V = \frac{4}{3} \pi a^2 c = \frac{4}{3} \pi a^3 \phi, \quad (2.163)$$

we get the new aspect ratio and $c$-axis length:
\[
\phi_{\text{new}} = \frac{V_{\text{new}}}{\frac{4}{3} \pi a_{\text{new}}^3}
\]

(2.164)

\[
c_{\text{new}} = a_{\text{new}} \phi_{\text{V60}}.
\]

Similarly, the new axis lengths and aspect ratio of a columnar (prolate spheroid) are

\[
c_{\text{new}} = \max(c, r),
\]

\[
\phi_{\text{new}} = \sqrt[3]{\frac{4 \pi c_{\text{new}}^3}{3 V_{\text{new}}}},
\]

(2.165)

\[
a_{\text{new}} = \frac{c_{\text{new}}}{\phi_{\text{new}}}.
\]

Figure 2.15: Schematic diagram of the change of aspect ratio due to riming. Shaded area denotes the rimed volume.
2. Heat Equations

One fundamental difference between the drop-drop interaction and the ice-drop interaction is that the latter involves a phase change. The surface of the ice crystal heats up during riming, owing to the release of latent heat from the freezing of drops. Such latent heating will influence the diffusional growth of ice particles and needs to be included in the heat transfer equation. The heat equation (2.155) for the diffusional growth can be extended as

\[
\frac{dH_i}{dt} = \left. \frac{dH_i}{dt} \right|_{\text{cond}} + h_w \frac{dm_i}{dt} \left|_{\text{cond}} \right. + \sum \left[ h_w \left. \frac{dm_i}{dt} \right|_{\text{rime}} \right],
\]

(2.167)

where \( h_w \) is the specific total heat of each drop, and \( \left. \frac{dm_i}{dt} \right|_{\text{rime}} \) is the mass accretion rate for each drop category. Note that the temperature of the ice is assumed to be uniformly distributed throughout the whole volume in this study.

2.3.4. Melting and Shedding

The latent heating of ice particles due to the accretion of the supercooled drops is balanced by the conduction of heat to the environmental air. As long as the temperature of the particle remains below 0°C, all accreted cloud water must freeze and the particle is considered to grow in the so-called dry-growth regime. During heavy riming, however, the released latent heat of freezing cannot be dissipated fast enough and part of the accreted water will remain unfrozen (Ludlam, 1950). The ice particle is then considered to grow in the wet growth regime with its surface temperature maintained at 0°C. Another growth mode that also has liquid water accumulated on the ice surface is the
melting of ice particle as it falls into an environment with air temperature higher than 0°C. The criterion for either the wet growth or melting to occur is

\[ h_i(T) > h_i(T_o) = 0, \quad (2.168) \]

where \( h_i \) is the specific total heat of the ice particle and \( h_i(T_o) \) is the specific total heat of ice at 0°C. This criterion simply means that if the total heat of the particle exceeds that of a bulk ice particle with the same mass at 0°C, the excess heat must be from the unfrozen part of the particle. The mass of the melt water can be derived easily by reexamining the total heat of the particle:

\[ H_i = m_w h_w(T_o) + m_i h_i(T_o), \quad (2.169) \]

where \( m_w \) and \( m_i \) are the liquid and solid portion of the mass, respectively. Since \( h_i(T_o) = 0 \) and \( h_w(T_o) = h_i(T_o) + l_f(T_o) = l_f(T_o) \), we have

\[ m_w = \frac{H_i}{l_f(T_o)}. \quad (2.170) \]

This melt water tends to fill in the available void spaces in the ice particle, which is called spongy growth. When no more porous space is accessible, melt-water will accumulate on the surface of the ice particle. Rasmussen et al. (1984) showed that wet ice particles that have ice-cores of diameter less than 9 mm tend to form a layer of water film over the ice surfaces while those with larger cores tend to form a water torus near the equator of the particles. The torus ring is a combined result of the tangential stress on the lower surface of the particle, which advects the melt-water upward, and the normal stress of the flow separation near the equator of the particle, which allows the meltwater to accumulate there due to gravity (Rasmussen et al., 1984). This water torus tends to increase the velocity shear and produce turbulence in the boundary layer near it. When the velocity shear exceeds a certain level, the balance between the stresses cannot be maintained, and
the melt water will *shed* from the particle’s surface to form liquid drops. Rasmussen and Heymsfield (1987) found that *shedding* will not occur unless the mass of the water is greater than the critical mass

\[ m_w^* = 0.268 + 0.1389 \, m_{\text{core}}, \quad (2.171) \]

where \( m_{\text{core}} \) is the mass (in g) of the ice core including the unfrozen part. However, only part of the meltwater will shed, and the amount of shedding depends on the size of the core and the mass of the water torus. We can find an empirical fit for the amount of shed water according to Figure 8 of Rasmussen et al. (1984):

\[ m_{\text{shed}} \sim m_w - \frac{m_t}{q}, \quad (2.172) \]

\[ q \equiv 1 + 10.67 \,(d - 0.9) - 10.81 \,(d - 0.9)^2 + 10.26 \,(d - 0.9)^3, \]

where \( m_t \) is the total mass of the particle and \( d \) is the diameter of the ice core in cm. The shedded water then turn into rain drops. The number and size distribution of the shedded drops are not well studied. Yet, we can adopt the spontaneous breakup scheme in determining the size distribution of the shedded drops.

Shedding does not necessarily occur only when the ice particles are soaked. Lesins and List (1986) pointed out there could be *spongy-shedding regime* and *dry-shedding regime* in addition to the *soaked-shedding regime*. These two types of shedding are not included in this study. The shedding of drops during melting is treated the same as the rime-shedding. The phenomenon similar to the *spongy-shedding* or *dry-shedding* could also happen during the melting of ice. Oraltay and Hallett (1989) observed water-shedding and ice-breakup during the melting of dendrites. However, it is assumed here that ice melts from the outer edge, and the melt water fills in the void spaces first before it accumulates on the ice surface.
Either from the wet growth or the melting process, the melt water that accumulates on the surface will alter the aspect ratio of the ice particle. According to Rasmussen et al. (1984), we can assume that melt water forms a layer of water film over the ice when the ice-cores are less than 9 mm in diameter. The aspect ratio of such ice particles is assumed to be the same as the ice core. For ice particles larger than 9 mm in diameter, the melt water will form a water torus. Figure 2.16 shows how the spheroidal shape is maintained in this study for such ice particles.

The melting of the ice particles, either wet or dry, is assumed to occur along the long axis. Such an arrangement is meant to simulate the melting of dendrites or needles from their tips first. Similar to the wet growth during riming, the melt water is assumed to fill up the void spaces first. The scheme for the change of aspect ratio is similar to that used for riming. This time, however, the length of the short axis is kept constant. The freezing of wet ice is taken to be exactly the opposite of the melting process.

### 2.3.5. Secondary Ice Production

There are three types of fragmentation processes that can occur during ice-phase hydrodynamic interactions and melting. The one that creates new liquid-phase particles (shedding) has been discussed previously. The other two processes that produce new ice particles are *rime-splintering* (Mossop et al., 1972) and *collision-fragmentation* (Hobbs and Farber, 1972; Vardiman, 1978). Ice particles generated via these two mechanisms are called *secondary ice*. The collisional and spontaneous fragmentation are not included in this study due to the lack of information. Three types of parameterization, generated according to different set of experimental data, can be used for the rime-splintering process. Koenig (1977), Gordon and Marwitz (1981), as well as Cotton et al. (1986),
Figure 2.16: Schematic diagram showing the aspect ratio of an ice particle with water torus. The shaded area represents the solid part of the particle.
used the experimental data from Hallett and Mossop (1974) to give the number of splinters produced for every milligram of rime accreted:

\[
J_{\text{splinter}} = 3.5 \times 10^5 \text{ g}^{-1} f(T) \left. \frac{dm}{dt} \right|_{\text{rime}}, \tag{2.173}
\]

where \( \left. \frac{dm}{dt} \right|_{\text{rime}} \) is the riming rate of the ice particle and \( f(T) \) is given by

\[
f(T) = \begin{cases} 
(T_i - 268.16) / 2, & 268.16 \leq T_i \leq 270.16 \\
(268.16 - T_i) / 3, & 265.16 \leq T_i \leq 268.16 \\
0, & \text{otherwise,}
\end{cases}
\]

where \( T_i \) is the surface temperature of the ice particle. The functional dependence shows a peak of secondary ice generation at about -5°C and minima above -3°C or below -8°C. Gorden and Marwitz (1981) and Cotton et al. (1986) used the data from Mossop (1976) to give the number of splinters produced for every 250 drops with diameter > 24 µm:

\[
J_{\text{splinter}} = \frac{1}{250} f(T) \left. \frac{dN}{dt} \right|_{\text{rime}}, \tag{2.174}
\]

where \( \left. \frac{dN}{dt} \right|_{\text{rime}} \) is the number of drops > 24 µm collected by the ice particles per second.

Gorden and Marwitz (1981) assumed that the production of ice splinters should also include drops with diameter ≤ 13 µm, according to Mossop (1978). Gorden and Marwitz (1981) showed that the second type of parameterization is better than the first type while the third type showed no improvement over the second type. Thus, the second type is used in this study.
2.4. Liquid-Phase Chemistry

Cloudwater not only can dissolve atmospheric aerosols and trace gases, but it also provides an alternate medium in which chemical transformations may proceed at rates many orders of magnitude greater than similar gas-phase reactions. The composition of cloudwater, in turn, affects the rates and equilibria of the aqueous-phase reactions and ultimately controls the spectral composition of rain.

There have been many cloud chemistry models that either assumed that an equilibrium is maintained between the gas and aqueous phase at all times (e.g., Hegg and Larson, 1990; Möller and Mauersberger, 1992). Walcek and Pruppacher (1984), Hill (1988), as well as Shimshock (1989) showed that Henry's law equilibrium does not always exist between droplets and the air. Other microphysical models that use the bulkwater approach assumed that the solute concentration is constant regardless of the drop size and origin (e.g., Flossmann et al., 1985; Taylor, 1989). Hill (1988), Ogren et al. (1989), Ayers and Larson (1990), as well as Chen and Lamb (1992a) showed that it is important to consider the drop-size dependent solute concentration, which cannot be accounted for in the bulkwater model. In this study, a more detailed approach is used for the liquid-phase chemistry, one that does not assume gas-liquid equilibrium or size-independent solute concentrations.
2.4.1. Equilibrium and Dissociation of Dissolved Trace-Gases

The balances between the gas-phase and liquid-phase concentrations are called the *Henry’s law equilibria*. The dissolved gas molecules usually combine with the water molecules and form hydrates, which will dissociate to a certain degree while interacting with the water molecules in the liquid. These equilibrium and dissociation reactions are quite fundamental (see Seinfeld, 1986, pp. 198-213) and will not be discussed further. Table 2.1 shows a list of the equilibrium and dissociation reactions and constants that will be used in this study. Although far from complete, these chemical species and reactions on the list are fundamental and educational at the present stage of study.

2.4.2. The Oxidation of S(IV) to form Sulfate

The oxidized form of sulfur, S(VI), is probably the most important trace chemical in the atmosphere that influences cloud formation and contributes to the cloudwater acidity (e.g., Lamb and Comrie, 1992). The source of S(VI) in liquid drops, aside from that introduced by the cloud-forming nuclei, is mainly from the oxidation of the dissolved S(IV) species. Two major oxidation pathways are the oxidation by H$_2$O$_2$ and by O$_3$. Seinfeld (1986, pp. 218-219) gives the reaction rate for the oxidation by H$_2$O$_2$ as

\[
\frac{d[S(IV)]}{dt} = \frac{k[H^+][HSO_3^-]}{1+K[H^+]}[H_2O_2], \quad (2.174)
\]

where $k=7.45\times10^7$ M$^{-2}$ s$^{-1}$, and $K=13$ M$^{-1}$ (temperature dependence unknown). For oxidation by O$_3$, we have:

\[
\frac{d[S(IV)]}{dt} = \{k_o[SO_2 \cdot H_2O] + k_1[HSO_3^-] + k_2[SO_3^-]\}[O_3], \quad (2.175)
\]

where, at 298K, $k_o=2.4\times10^4$ M$^{-1}$ s$^{-1}$, $k_1=3.7\times10^5$ M$^{-1}$ s$^{-1}$, $k_2=1.5\times10^9$ M$^{-1}$ s$^{-1}$. 
Table 2.1: Reactions of trace gas dissociation in water and the reaction constants. The temperature dependence of the equilibrium constant $K$ is expressed as

$$K = K_{298} \exp[-\frac{\Delta H}{R} (\frac{1}{T} - \frac{1}{298})].$$

<table>
<thead>
<tr>
<th>equilibrium reactions</th>
<th>$K_{298}$</th>
<th>$-\frac{\Delta H}{R}$, $K$</th>
<th>references</th>
</tr>
</thead>
<tbody>
<tr>
<td>1    $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$</td>
<td>$1.0 \times 10^{-14}$ [M$^2$]</td>
<td>-6710</td>
<td>S&amp;M</td>
</tr>
<tr>
<td>2    $\text{CO}_2(g) \rightleftharpoons \text{CO}_2 \cdot \text{H}_2\text{O}$</td>
<td>$3.4 \times 10^{-2}$ [M atm$^{-1}$]</td>
<td>2420</td>
<td>S&amp;M</td>
</tr>
<tr>
<td>3    $\text{CO}_2 \cdot \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$</td>
<td>$4.46 \times 10^{-7}$ [M]</td>
<td>-1000</td>
<td>S&amp;M</td>
</tr>
<tr>
<td>4    $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^-$</td>
<td>$4.68 \times 10^{-11}$ [M]</td>
<td>-1760</td>
<td>S&amp;M</td>
</tr>
<tr>
<td>5    $\text{SO}_2(g) \rightleftharpoons \text{SO}_2 \cdot \text{H}_2\text{O}$</td>
<td>1.23 [M atm$^{-1}$]</td>
<td>3120</td>
<td>S&amp;M</td>
</tr>
<tr>
<td>6    $\text{SO}_2 \cdot \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HSO}_3^-$</td>
<td>$1.23 \times 10^{-2}$ [M]</td>
<td>1960</td>
<td>S&amp;M</td>
</tr>
<tr>
<td>7    $\text{HSO}_3^- \rightleftharpoons \text{H}^+ + \text{SO}_3^-$</td>
<td>$6.61 \times 10^{-8}$ [M]</td>
<td>1500</td>
<td>S&amp;M</td>
</tr>
<tr>
<td>8    $\text{NH}_3(g) \rightleftharpoons \text{NH}_3 \cdot \text{H}_2\text{O}$</td>
<td>75 [M atm$^{-1}$]</td>
<td>3400</td>
<td>H&amp;D</td>
</tr>
<tr>
<td>9    $\text{NH}_3 \cdot \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{NH}_4^+$</td>
<td>$1.75 \times 10^{-5}$ [M]</td>
<td>-450</td>
<td>S&amp;M</td>
</tr>
<tr>
<td>10   $\text{H}_2\text{SO}_4(aq) \rightleftharpoons \text{H}^+ + \text{HSO}_4^-$</td>
<td>1000 [M]</td>
<td>$\uparrow$</td>
<td>P</td>
</tr>
<tr>
<td>11   $\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$</td>
<td>$1.02 \times 10^{-2}$ [M]</td>
<td>2720</td>
<td>S&amp;M</td>
</tr>
<tr>
<td>12   $\text{O}_3(g) \rightleftharpoons \text{O}_3(aq)$</td>
<td>$1.13 \times 10^{-2}$ [M atm$^{-1}$]</td>
<td>2300</td>
<td>KC&amp;H</td>
</tr>
<tr>
<td>13   $\text{H}_2\text{O}_3(g) \rightleftharpoons \text{H}_2\text{O}_2(aq)$</td>
<td>$7.45 \times 10^4$ [M atm$^{-1}$]</td>
<td>6620</td>
<td>L&amp;K</td>
</tr>
</tbody>
</table>


$\uparrow$ temperature dependence unknown.
2.4.3. Kinetics of Mass Transport between Liquid and Gas phases

The amount of dissolved gases in the liquid is controlled by the mass transport kinetics. The Henry's law equilibrium used in conventional cloud chemistry models might not be reached, especially when the cloud droplets are experiencing rapid growth. Therefore, the kinetic mass transport approach is used in this study for the gas absorption and desorption by cloud droplets.

The Maxwell two-stream equation for the diffusional growth of droplets and ice particles mentioned previously can also be applied to the absorption or desorption of trace gases into the liquid. Because the dissolved trace gases normally do not contribute to the size of the drop, the interfacial mass transport equation can be simplified so that an analytical solution can be obtained. For the absorption of gas species $j$, it can be written as

$$\frac{dm_j}{dt} = 4\pi r D_j N_{Sh,j} (\rho_{j,\infty} - \rho_{j,r})$$, \hspace{1cm} (2.176)

where $m$ is the mass in the liquid phase, $r$ the drop radius, $D$ the diffusion coefficient of gas in air, $N_{Sh}$ the mass ventilation coefficient (Sherwood number), $\rho_{j,\infty}$ the gas molar density in the environment, and $\rho_{j,r}$ the gas molar density at the drop surface. By assuming that the drop is well mixed and that the temperature at the surface of the drop is the same as that of air, the gas density at the drop surface, $\rho_{j,r}$, can be expressed as

$$\rho_{j,r} = \frac{P_j^*}{R T}$$, \hspace{1cm} (2.177)

where

$$P_j^* = \frac{[j]}{H_j^*}$$ \hspace{1cm} (2.178)
is the potential partial pressure (may need to consider curvature effect) of the dissolved gas, $[j]$ is the concentration of gas $j$ in the liquid and $H_j^*$ the modified Henry’s law coefficient for dilute solutions. Converting the mass of the chemical in the drop into concentration, the mass transfer equation can be rewritten as

$$\frac{d[j]}{dt} = \frac{3D_{j}^{\text{N_sh,j}}}{r^2 R \cdot T} \left( P_j \cdot \frac{[j]}{H_j^*} \right). \quad (2.179)$$

Thus, the rate of interfacial mass transfer is determined by the difference between the concentrations in the two phases -- partial pressure and potential partial pressure. It is useful to express this equation in terms of the species $j$ in the liquid-phase per mole of air:

$$\frac{dy_j}{dt} = g_j - \xi_j y_j, \quad (2.180)$$

where $y_j$ is the molar mixing ratio of the aqueous-phase species concentration in air, $g_j$ is the generation rate of species $j$, and $\xi_j$ is the decay rate coefficient. Comparing the previous two equations, we have

$$y_j = [j] L_r = [j] N_r \frac{4\pi r^3}{3}, \quad (2.181)$$

where $L_r$ and $N_r$ are the volume and number of drops with radius $r$ per mole of air,

$$g_j = \frac{3D_{j}^{\text{N_sh,j}} P_j}{r^2 T} L_r = \frac{4\pi r N_r}{T} D_{j}^{\text{N_sh,j}} P_j, \quad (2.182)$$

$$\xi_j = \frac{3}{r^2 R \cdot T} \frac{D_{j}^{\text{N_sh,j}}}{H_j^*}. \quad (2.183)$$
The dissolved gases normally do not contribute to the drop size. Equation (2.180) is thus a linear differential equation of order one and can be solved analytically as

$$y_j = \frac{g_j}{\xi_j} + \left(y_{j,0} - \frac{g_j}{\xi_j}\right)e^{-\xi_j t}, \quad (2.184)$$

where $y_{j,0}$ is the initial mixing ratio of $j$. Such an analytical solution is not available for the sorption (condensation) of water vapor onto the drops because of the size dependence. As will be shown in Section 3.5.2, an analytical solution such as this is very useful for solving a set of ordinary differential equations that are stiff.

For small drops, it is important to consider the free-molecular effect for the diffusion of gas molecules to a sphere (Jacob, 1986). To account for the free molecular effect, the mass transfer rate should be modified by the factor $\eta$, which is a function of the Knudsen number $N_{Kn}$ and the sticking coefficient $\alpha_j$ (Slinn, 1984):

$$\eta = \left\{1 + \left[1.33 + 0.71N_{Kn}^{-1} + \frac{4(1 - \alpha_j)}{3\alpha_j}\right]N_{Kn}^{-1}\right\}^{-1}. \quad (2.185)$$

We can combine $\xi_j$ and $\eta$ as $\xi_j^* = \xi_j \eta$.

Some diffusion coefficients for trace gases in air are listed in Table 2.2. From Chapman-Enskog’s theory for the binary diffusivity (Chapman and Cowling, 1970), the diffusivity of species A in media B is

$$D_{AB} = \frac{3}{8\pi} \sqrt{\frac{k^3 T^3 (1 + z)}{2m_A P\sigma_{AB}^2 \Omega_{AB}^{(1,1)}}}, \quad (2.186)$$

where $k$ is Boltzmann’s constant, $m_A$ and $m_B$ the molecular weights of A and B, $z = m_A/m_B$, $\sigma_{AB} = (\sigma_A + \sigma_B)/2$ is the average diameter, and $\Omega_{AB}^{(1,1)}$ the collision integral.
dependence of the diffusion coefficient on temperature and pressure is evident from the above equation, and can be expressed as (Schwartz, 1986)

\[ D = D_o \left( \frac{T}{T_o} \right)^\alpha \frac{P}{P_o}, \]  

(2.187)

where subscript “o” denotes values at a reference state, and \( \alpha \) ranges from 1.75 to 2. The values of \( \alpha \) for each species are also listed in Table 2.2. The diffusion coefficients for ozone and hydrogen peroxide are not available. We thus apply the Chapman-Enskog's first approximation of the diffusion coefficient for a binary mixture (Hirschfelder et al., 1954),

\[ D_{AB} \propto \frac{m_x + m_y}{m_x m_y}, \]  

(2.188)

to get the diffusion coefficient for O\(_3\) and H\(_2\)O\(_2\), using SO\(_2\) and O\(_2\), respectively, as the reference species.
Table 2.2: Diffusion coefficients for various gases.

<table>
<thead>
<tr>
<th>species</th>
<th>D, cm$^2$ s$^{-1}$</th>
<th>$T$, °C</th>
<th>$\alpha$</th>
<th>references</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>0.211</td>
<td>0</td>
<td>1.94</td>
<td>Hall and Pruppacher, 1976</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0.181</td>
<td>0</td>
<td>1.75</td>
<td>Phys. Handbook</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0.674</td>
<td>0</td>
<td>1.75</td>
<td>Phys. Handbook</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.139</td>
<td>0</td>
<td>2</td>
<td>CRC Handbook</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>0.126</td>
<td>25</td>
<td>1.75</td>
<td>Schwartz, 1986</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>0.234</td>
<td>25</td>
<td>1.75</td>
<td>Schwartz, 1986</td>
</tr>
<tr>
<td>O$_3$</td>
<td>0.14</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>0.20</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$SO$_2$</td>
<td>0.112</td>
<td>25</td>
<td>1.75</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0964</td>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\textcircled{1}$ values derived from Chapman-Enskog first approximation.
2.5.  Ice-Phase Chemistry

The chemistry that occurs in the ice-phase is often thought to be less important than that in the liquid-phase, and is ignored in most cloud chemistry models. Yet, there is increasing evidence showing that the ice-phase chemistry cannot be totally neglected. Chen and Lamb (1990) showed that the removal of S(IV) by the ice-phase precipitation can be as much as 10% of that by the liquid-phase precipitation. The observational result of Borys et al. (1988) showed that the average trace chemical concentration ratios of snow water to cloud water can be greater than one. Also, it has been strongly suggested that heterogeneous chemical reactions occurring in ice clouds might be responsible for the polar stratospheric ozone depletion (Toon et al., 1989; Turco et al., 1989). Therefore, it becomes essential for a complete cloud chemistry model to include the ice-phase chemistry. In this section, we will focus on the physical processes that control the removal of trace chemicals by the ice-phase precipitation. The chemical reactions occurring in the ice-phase are potentially important but are not included at this stage due to their complicated nature and the general lack of information.

2.5.1.  The Sorption of Trace Gases onto Ice Particles

The diffusion process not only occurs between the gas and liquid phases but also between the gas and ice phases in the clouds. Although solute tends to be excluded from the bulk ice (Gross, 1968) and remain on the surface of ice particles, the large surface-to-volume ratio makes ice particles a potentially good candidate for removing trace chemicals from the air. When ice particles are growing by vapor deposition, the
adsorbed trace gases can even be buried and incorporated into the bulk ice (Valdez et al., 1989).

There are not many experimental studies being conducted to explore the sorption of trace gases onto ice. However, Sommerfeld and Lamb (1986), as well as Clapsaddle and Lamb (1989), have studied the sorption of SO$_2$ onto non-growing ice at various temperatures. Valdez et al. (1989) did a similar experiment on ice growing by vapor deposition but at only one temperature. Chen and Lamb (1990) compiled the results from Clapsaddle and Lamb to give the following surface sorption concentration as:

$$\left[\text{S(IV)}\right]_{\text{surf}}^{\text{sorp}} = 8.5 \times 10^5 \text{ mol m}^{-2} \text{ atm}^{-1/2} \exp\left(\frac{-5.272 \times 10^3 \text{K}}{T}\right)P_{\text{SO}_2}^{1/2}, \quad (2.189)$$

and the result from Valdez et al. (1989) to give the volume sorption concentration as:

$$\left[\text{S(IV)}\right]_{\text{vol}}^{\text{sorp}} = 0.282 \text{ M atm}^{-1/2}P_{\text{SO}_2}^{1/2}, \quad (2.190)$$

where $P_{\text{SO}_2}$ is the partial pressure of SO$_2$ in atm. The sorption concentrations for other trace chemicals, as well as the interactions between them, are not well known and need further experimental studies.
2.5.2. The Entrapment of Volatile Trace Chemicals during Riming

Ice particles can collect not only water but also the solute in the cloud drops during riming. Yet, during the riming process, volatile trace chemicals that were originally dissolved in the droplets tend to expelled from the frozen drop. During slow freezing, the amount of each gas that remains in the ice is determined by its solubility, which is normally much lower than that in the liquid. However, during the riming process, the impacting cloud drops freeze rapidly, particularly for small drops at large degrees of supercooling (see Section 2.3.3). The fast propagation of ice within the freezing drops may result in the physical entrapment of the dissolved gases. Past studies of gaseous entrapment in freezing water drops have been sparse. Lamb and Blumenstein (1987) conducted experiments with droplets in the range of a few to 10 µm diameter impinging at 2 m s\(^{-1}\) to form rime at temperatures between 0 and -20\(^\circ\)C. They found that the fraction of solute retained during freezing (the entrapment or the retention coefficient) for S(IV) can be expressed by the empirical expression

\[
\hat{f}_{S(IV)} = 0.012 + 0.0058 \Delta T, \tag{2.191}
\]

where \(\Delta T\) is the drop supercooling, 273.15 - \(T_w\). Iribarne and Pyshnov (1990) measured a retention coefficient for S(IV) as

\[
\hat{f}_{S(IV)} = 0.25 + 0.012 \Delta T \tag{2.192}
\]

for droplets falling through a stagnant atmosphere;

\[
\hat{f}_{S(IV)} = 0.52 + 0.002 \Delta T \tag{2.193}
\]

for a sample collected under ventilation with jet arrangement; and

\[
\hat{f}_{S(IV)} = 0.78 - 0.008 \Delta T \tag{2.194}
\]
for sample collected under ventilation with rotating rods. The above results do not have high correlation and are not quite consistent with each other. The discrepancies could conceivably result from the different drop sizes and riming rates used in the different sets of experiments.

Iribarne et al. (1990) measured the retention of HCl, HNO₃, NH₃, and H₂O₂, and found that these chemicals were totally retained in the ice after freezing. However, Snider et al. (1992) found that the retention coefficients for H₂O₂ were always less than unity (\( f_{H_2O_2} = 0.24 \pm 0.07 \)) in natural clouds. Corrections to account for the rapid reactions between the dissolved H₂O₂ and S(IV) increase the retention coefficient to only 0.30. They suggested that the freezing rates in the laboratory study of Iribarne et al. (1990) are too high and that some H₂O₂ is released to the gas phase during riming in natural clouds.

### 2.6. Summary

The material introduced in this chapter constitutes the theoretical basis for the microphysical and chemical processes that are to be simulated in this study. The microphysical processes included are quite detailed because of the highly interactive roles they play in cloud and precipitation formation. The liquid-phase chemistry included is quite simple, but it is nevertheless enough to provide some insight into the cloud effect on the atmospheric trace chemicals as well as the role of chemistry in the formation of clouds. Ice-phase chemistry is generally not well studied and lacks many of the needed theoretical and experimental studies. Here, we are able to include some of the laboratory results, which have not been used in numerical simulations of this kind. Gas-phase chemistry (photochemistry) and radiative transfer are both quite important to the cloud processes, but they are not essential to the current topic.
Chapter 3

NUMERICAL METHODS

Numerical simulation of cloud microphysics and chemistry is very complicated and requires a variety of techniques. The number of variables needed to describe the physical and chemical properties for each cloud particle is often more than that for the pure gas-phase or dynamic type calculations. The difficulties in the bookkeeping of these variables are multiplied by the numerous microphysical and chemical processes involved. The accuracy and efficiency in the simulation of such complex systems depend very much on the applied numerical techniques. In this chapter, some numerical techniques that are essential to this study will be introduced.

3.1. Multi-Component Particle Framework and Bin Methods

From a macroscopic point of view, the atmosphere can be regarded as a locally uniform system. In dynamic models, it is conventional to subdivide the atmosphere into finite grid spaces and treat each portion as a homogeneous mixture. When microscopic entities such as aerosol and cloud particles are the main subject of study, however, the atmosphere can no longer be considered homogeneous. Each atmospheric particle itself defines a system of unique physical and chemical properties. Such systems are by no means less complicated than the embedding gas-phase system. The evolution of these particles must be calculated independently from that for the bulk gas-phase. This section describes the particle framework and the bin methods that are used in dealing with the growth and decay of atmospheric particles.
3.1.1. Bin Concept

The evolution of atmospheric particles in size or composition usually cannot be solved analytically. Two basic methods are often used to resolve the complexity of the evolution of atmospheric particles -- the particle-tracing method and the *bin method*. The particle-tracing method, which keeps track of the history of individual particles, is not realistic for cloud modeling because of its limitation in handling a large population of particles. Young (1974a) also pointed out that the particle tracing method encounters computational difficulties in multi-layer models and is not suitable for Eulerian spatial frameworks. Besides, it is very difficult to deal with a realistic population of atmospheric aerosols with the particle-tracing method simply due to the large number and variety of particles that exist.

The *bin methods* group particles of similar properties into representative "bins" to reduce the particle population to a manageable number of systems. The *total particle number* in each bin category is introduced as the grouping parameter. The value of the properties in each bin component is restricted to be within a uniquely specified range. However, it is not necessary to categorize the particles according to every physical and chemical property of the particles. Conventional cloud microphysical models use only the mass or size of the particles as the categorization parameter (the bin component). Properties that are not categorized (such as temperature, density, etc.) are essentially one-category components, which have unlimited value ranges. However, in order to study the cloud processes in more detail, it is sometimes necessary to categorize cloud particles according to more than one property of the particles. We may call those properties that are to be categorized the *major properties* (e.g., water mass, solute mass, and the shape of ice particles). The properties that are considered to be minor are those which stay fairly constant (e.g., particle temperature, density, etc.) or those that are not influential to the
main cloud processes (e.g., dissolved trace gases). Detailed categorization on such properties will only encumber the computation without gaining more information.

Two objectives that are emphasized in this study are the chemistry and ice-phase microphysics in clouds. In order to study the effect of solute on the cloud processes, a solute-mass component is used in addition to the water-mass component in this study. Normally, sulfate is used to represent the major solute in cloud particles. Thus, for the liquid-phase particles, the particle framework is two-dimensional with water-mass and sulfate-mass as its two components. In maritime simulations, a sodium-chloride component can be applied either in place of or in addition to the sulfate component. The representation of ice-phase particles requires a separate framework. One physical parameter that distinguishes the ice-phase particles from that in the liquid-phase is their numerous possible shapes, which has significant importance to the microphysics and chemistry occurred in the clouds. Thus, a shape-factor (axial ratio) is included in the ice-particle framework in addition to those used in the liquid-phase particle framework. Although a single shape-factor is not sufficient to describe the complicated features of ice, it is already a great improvement over the existing cloud models to have more than one bin component.
3.1.2. Historical Review of Various Bin Methods

1. Lagrangian Framework versus Eulerian Framework

In dealing with the particle frameworks with large dimensions, it is necessary to apply numerical schemes that conserve properties and, in the mean time, perform fast and accurate calculation of the evolution of particle spectra. There are generally two types of bin-methods for cloud microphysical simulations. The first type is those employed in the Lagrangian computational framework, as used by Fitzgerald (1974), in which the bins evolve along with the particles. For simple processes such as condensation growth, a Lagrangian framework works very well since there will be no numerical diffusion. However, for more complicated processes such as collision-coalescence growth that leads to new particle groups, the Lagrangian framework is inadequate. The Lagrangian framework is similar to the particle-tracing method in a way that the number of particle groups increases with the creation of new particles, which makes it too expensive to deal with. The second type of bin method is based on an Eulerian framework, in which the bin limits are fixed. The evolution of particles then result in the transfer of particles between bins.

2. Eulerian Bin Methods

Figure 3.1 shows four types of Eulerian bin methods commonly used in cloud modeling -- the discrete, semi-discrete, semi-continuous, and continuous bin methods. In the calculation of the growth or decay of particles, the bin-properties and the total number are frequently transferred between bins. In the discrete bin method, the mean bin-property is generally fixed (Figure 3.1a). To maintain this constant mean value, one would either unrealistically readjust the total number of particles in the current bin or transfer particles into other bins. To conserve both mass and number and, in the
meantime, realistically transfer particles between bins without numerical diffusion has been a major problem for cloud microphysical simulations. Berry (1967), Berry and Reinhardt (1974), Gelbard and Seinfeld (1978), as well as Flossman et al. (1985) applied the scheme that solves the number distribution function at the grid points. Values of the function between grid points are interpolated using Lagrange polynomials or cubic spline polynomials. However, these methods do not conserve number and mass and are computationally intensive. Bleck (1970), Danielson et al. (1972), and Soong (1974) used a mass-weighted mean value for the drop number density in their discrete bin model. Although not set to be at the mid-point of the bin, the nominal bin size in their scheme is still fixed. Since only mass is conserved, such a technique is called a one-moment method.

Figure 3.1: Four types of bin method. (a) discrete method, fixed value; (b) semi-discrete method, variable single value; (c) semi-continuous method, rectangular or normal distribution but bin not filled; and (d) linear continuous bin.
In the *semi-discrete bin method*, the average drop size within a bin can vary during the growth and, therefore, the number and mass are conserved (Figure 3.1b). However, the average drop size may occasionally grow beyond the bin limits. If all particles are transferred into the next bin in such cases, the original bins may suddenly be left without any particles. Therefore, "holes" will be created in the supposedly continuous distribution. Such problems are usually accompanied by severe numerical diffusion.

The *semi-continuous bin method* is designed to deal with the empty-bin problem by assuming some distribution function for the particles in the bin, then transferring those particles that have grown beyond the bin limits into the neighboring bins (Figure 3.1c). Egan and Mahoney (1972) used a "grid-element model" to study the pollution-transport problems. In order to minimize the pseudo-diffusion associated with the numerical advection, they applied more than one moment of the pollutant distribution within a grid element. Their techniques involve retaining and conserving higher moments of a distribution within each category and have been adopted by Ochs and Yao (1978) for the study of advection problems. However, because it was originally designed to retain subgrid-scale information for line- or point-source emissions, this technique implies discontinuities in the distribution function. The assumed distribution, although continuous in nature, does not necessarily occupy the whole bin and may extend over the neighboring bins. Tzivion et al. (1987) pointed out that one of the limitations of the method is the requirement of an unreasonably short time increment for the purely stochastic treatment of collection.

The *continuous bin method* assumes a more realistic continuous distribution that extends over the entire bin (Figure 3.1d). Young (1974a) developed an easy to use and conceptually easy to understand bin method, which assumes a linear distribution function
within a bin. Knowledge of the total number and bin-property value allows the linear distribution function to be determined from the law of conservation. The growth of the particles then results in the displacement of the distribution along the bin-axis. Particle transfer between bins due to growth is then possible by shifting the portion that "spilled" over into the appropriate neighboring bins. The continuous-bin method is conceptually similar to the method-of-moments proposed by Stieltjes (1894) and Golovin (1963), which is discussed next.

3. Method-of-moments

Drake (1972), Enukashvilly (1980), Tzivion (1980), Tzivion et al. (1987), as well as Feingold et al. (1988) applied the method-of-moments to conserve two or more moments of the particle spectrum while minimizing the use of the approximate distribution functions in obtaining analytical solutions for the integration of the growth equations. In order for the method to work, the functional form of the growth kernel must exist and preferably in the form of polynomials. The introduction of the polynomials, however, creates higher order moments and generates a closure problem for the set of equations, which then needs a certain degree of approximation. A linear approximation to the number distribution functions is needed when the domain of integration does not span the whole category, and the zeros of the approximation function must be found in the case of a negative distribution function. The method-of-moments is much more efficient and requires fewer bins than Bleck's (1970) one-moment method. Yet, it normally cannot be generalized for different collection kernels, different bin-components, or non-logarithmically sized bins. Recently, Tzivion et al. (1992) made an effort to generalize the method-of-moments so that an irregular bin-sizing factor can be used.
3.1.3. The Hybrid Bin Method

The *hybrid bin method* proposed and used in this study is a combination of the *semi-discrete method* and the *continuous bin method*. The amount of growth is calculated using the semi-discrete method. The continuous bin method is then used for the transfer of particles between bins. The *continuous bin method* consists of two parts: 1) the linear distribution function, and 2) the bin-shift procedure. Such an arrangement vastly simplifies the computer algorithm and reduces the computational time compared with the method-of-moments, which applies the distribution function in the calculation of particle transfer between bins. The *hybrid bin method* has most of the advantages of those aforementioned techniques, and is easy to use and conceptually easy to understand.

3.1.3.1. The Sub-Grid Linear Distribution Function

The *continuous bin method* is an extension of Young's (1974a) method, which allows the number density of particles within a bin to be a function of mass when mass growth is considered, and a function of height when sedimentation is considered. The number density function, as shown in Figure 3.2, is assumed to be linear within a bin and is expressed as:

\[ n(x) = n_o + k (x - x_o), \]  

(3.1)

where \( x \) is the independent variable of the number density function (can be log radius, mass, height, etc.), \( n_o \) is the number density at the midpoint \( x_o \) of the bin, and \( k \) is the slope of the distribution function. From the conservation of the two moments, the total number \( N \) and the total bin-property \( M \), we have
\[ n(x) = n_0 + k \left( x - x_0 \right) \]

Figure 3.2: Linear distribution function of two moments.

\[ N = \int_{x_1}^{x_2} n(x) \, dx , \quad (3.3) \]

\[ M = \int_{x_1}^{x_2} x \, n(x) \, dx , \quad (3.4) \]

where \( x_1 \) and \( x_2 \) are the lower and upper limits of the bin, and \( x \) is the bin-property.

Take the most frequently considered property -- mass -- as an example, \( M \) is then the total particle mass in the bin. Although mass is used as the representative property (\( x \)) in later discussions, it is important to realize that \( x \) can be any other particle property such as size, solute content, shape, or one of several spatial variables. The details about the implementation of the bin method on various properties is given in Section 3.1.3.7. If (3.1) is inserted into (3.3) and (3.4), we can derive \( n_0 \) and \( k \) as:

\[ n_0 = \frac{N}{x_2 - x_1} , \text{ and } k = \frac{12(M - x_0 N)}{(x_2 - x_1)^3} , \quad (3.5) \]

where \( x_0 = \frac{x_1 + x_2}{2} \). The conservation of \( N \) and \( M \) is thus implied in the number density function, which can readily be used for calculations that involve particle spectra. By
way of example, Figure 3.3 demonstrates how the linear distribution function approximates a sinusoidal curve.

1. **Positiveness of the Distribution Function**

The linear number density function does not always satisfy the condition of positiveness throughout the bin interval. The distribution function may become partially negative (see Figure 3.4a). This happens most often at the tail-end of the overall spectrum, whenever the average size of the particles is close to either of the bin limits. Violation of the positiveness will lead to unrealistic negative numbers of particles as well as some numerical diffusion. Enukashvilly (1980) treated the problem by applying a zeroth-order approximation function, which forces the distribution function to be zero at the initially negative end, as shown in Figure 3.4b. To be more realistic, however, the distribution function should be allowed to occupy only part of the bin, as demonstrated in Figure 3.4c. Thus, once either \( n(x_1) \) or \( n(x_2) \) is found to be less than zero with the \( k \) and \( n_o \) derived previously, one should modify the distribution function as:

\[
n(x) = k_* (x - x_*) .
\]  

(3.6)

The parameters \( x_* \) and \( k_* \) can be derived by inserting this modified distribution function back into (3.3) and (3.4):

\[
x_* = \frac{3M}{N} - 2x_2 , \quad k_* = \frac{2N}{(x_2 - x_*)^2} , \quad \text{for } n(x_1) < 0,
\]

\[
x_* = \frac{3M}{N} - 2x_1 , \quad k_* = \frac{-2N}{(x_1 - x_*)^2} , \quad \text{for } n(x_2) < 0.
\]
Figure 3.3: First-order approximation of the curve $n(x) = \sin(x) + 1$ using the continuous-bin method.

Figure 3.4: Positiveness of the linear distribution function: (a) before adjustment; (b) Enukashvilly's zeroth-order approximation; (c) method proposed here.
2. High-order distribution functions

In the previous section, the distribution function was assumed to be linear (3.1), and the parameters \((n_o, k)\) were shown to be specified by conserving the zeroth and first moments (i.e., the number and the mass, respectively). However, it is possible to utilize higher-order approximations even though only the first two moments are known. Figure 3.3 showed that the first-order distribution functions are not necessarily connected at the boundaries the bins. In reality, the whole spectrum should be a smooth function. By forcing the inter-bin distributions to be connected, we obtain boundary conditions for the derivation of second-order distribution functions. Higher-order approximations can be similarly obtained by forcing the first, second, and higher derivatives of the distribution function to be continuous at the bin limits. The Piecewise Parabolic Method of Carpenter et al. (1990) is an example of a second-order scheme. Note that this Piecewise Parabolic Method, initially developed in astrophysics for modeling fluid flows with strong shocks and discontinuities, was successfully adapted for treating sharp gradients in small-scale meteorological flows.

High-order schemes usually give higher accuracy in the expense of computational resources. A low-order scheme may provide the same accuracy as that from the high-order schemes by using higher bin resolution. It is not easy to find the optimal balance between the order of the distribution function and the bin resolution for a particular application. However, the first-order scheme is quite flexible and easy to apply. As will be mentioned later, the hybrid bin-method developed here may be applied to any bin-sizing arrangement. Changing the bin size does not require the change of program coding (not true for the method-of-moments). This is not possible, however, if one needs the flexibility to select the order of the distribution function. Some examples will be given later to show that the first-order approximation is appropriate for this study.
3.1.3.2. **Semi-Discrete Growth Scheme**

With the linear distribution function (3.1), the total mass growth rate within any bin is simply expressed in terms of the particle growth rates as (cf., equation B29 of Tzivion et al., 1989)

\[
\frac{dM}{dt} = \int_{x_1}^{x_2} \frac{dx}{dt} n(x) \, dx. \tag{3.7}
\]

Here, \(x_1\) and \(x_2\) are the moving boundaries of the distribution function, which change with time; \(\frac{dx}{dt}\) is the mass growth rate of particles with mass \(x\), and is often called the *growth kernel* when used in the above integral form. In order to integrate this equation, the growth kernel \(\frac{dx}{dt}\) must be an explicit function of \(x\). Tzivion et al. (1989) derived an analytical solution to this equation for a simple growth kernel of \(\frac{dx}{dt} \propto x^{1/3}\). However, when \(\frac{dx}{dt}\) is a high-order polynomial or transcendental function, this integration is often not easy to evaluate. To avoid such a problem, one may separate the growth calculation from the particle transfer scheme. This is done by first applying the *semi-discrete bin method*, which assumes all particles in the bin have the same average properties, to calculate the total growth. In other words, we use the 'growth of the mean' to represent the 'mean growth'. Of course, there will be some error associated with such an approximation. As will be shown in Section 3.1.4, the semi-discrete growth rate is quite accurate for small enough bin sizes. A modification factor is available to count for any non-linearity. After we calculated the total growth, the particle transfer between bins is then performed using the bin-shift method described below. This hybrid scheme can vastly reduce the complexity of the governing equations and the computational time.
3.1.3.3. Continuous (Lagrangian) Bin-Shift Methods

Bin-shift is conceptually very similar to advection on Eulerian coordinates. If component variable $x$ is the distance, the growth rate $\frac{dx}{dt}$ would then be the advection velocity. The bin-shift is done by first calculating the growth (advection) in a Lagrangian coordinate, then perform "Eulerian remapping" to put the distribution function back into the original coordinate. Normally, one would derive the linear distribution function that occurs "before" the growth, as done by Young (1974a). However, one of the advantage of separating the growth scheme from the bin-shift scheme is that we can alternatively assume that the distribution function is linear "after" the growth. We will call the former the *pre-growth linear method* and the latter the *post-growth linear method*.

1. The Pre-growth Linear Method

In the pre-growth linear method, a linear distribution function is derived using the total number and mass before the growth and the distribution function is assumed to maintains its linearity during the growth. In order to maintain the original slope of the distribution, however, one must assume that every particle in the bin grows at the same rate. Such an assumption is appropriate only when the growth rate $\frac{dx}{dt}$ is independent of $x$. While the total number is kept constant, the new total mass $M'$, lower bin-limit $x'_1$, and upper bin-limit $x'_2$ are now changed to

$$M' = M + N\delta x = M + \delta M,$$
$$x'_1 = x_1 + \delta x,$$
$$x'_2 = x_2 + \delta x,$$

where $\delta M$ is the total growth and $\delta x$ is the mean growth. As shown in Figure 3.5, part of the distribution may exceed the bin limits and the particles in it should be transferred
to the next bin as appropriate. The number and mass that need to be transferred can be
determined by the following functions:

\[
\Delta N = N(n_0, x_0, k, x_2, x_2'), \quad \Delta M = M(n_0, x_0, k, x_2, x_2'), \quad \text{for } \delta x > 0
\]
\[
\Delta N = N(n_0, x_0, k, x_1, x_1'), \quad \Delta M = M(n_0, x_0, k, x_1, x_1'), \quad \text{for } \delta x > 0
\]

where the functions \( N \) and \( M \) are expressed as

\[
N(n_0, x_0, k, x_a, x_b) \equiv \int_{x_a}^{x_b} n(x) \, dx = (x_b - x_a)n_0 - k\left(x_0 - \frac{x_b + x_a}{2}\right),
\]
\[
M(n_0, x_0, k, x_a, x_b) \equiv \int_{x_a}^{x_b} x \, n(x) \, dx = n_0 \frac{x_b^2 - x_a^2}{2} + k\left(\frac{x_b^3 - x_a^3}{3} - x_0 \frac{x_b^2 - x_a^2}{2}\right).
\]

Now, what if the growth equations are non-linear with respect to \( x \)? The shifts
of the two bin-limits and the mean may not be exactly the same and the distribution
function may become nonlinear after growth. A straightforward linear bin-shift does
not always provide for an accurate calculation. This problem can be avoided by
applying the post-growth linear method.

Figure 3.5: Bin-shift of the pre-linear distribution function: (a) growth and (b) decay.
Note that the two bin-limits shifted by the same amount.
2. The Post-growth Linear Method

The first-order approximation works equally well on a post-growth distribution and on a pre-growth distribution. The new total mass of the post-growth distribution is derived from the decoupled semi-discrete scheme. In contrast to the pre-growth linear method, we now have the freedom of deciding the two new bin-limits. For a constant growth rate $\frac{dx}{dt}$, this method is the same as the pre-growth linear method. If $\frac{dx}{dt}$ is known, the shift of the new bin limits $\delta x'_1$ and $\delta x'_2$ can be calculated in the same way as $\delta x$ is calculated, but separately. The new distribution function (see figure below) can then be derived from the new total mass, total number, and the two new bin limits $x'_1 = x_1 + \delta x'_1$ and $x'_2 = x_2 + \delta x'_2$. Notations in (3.9) are still valid for the bin-shift with the post-growth method.

Figure 3.6: Schematic diagram of the post-growth linear method. Note that the two bin-limits shift by different amount.
3. Positiveness Check for Bin-shift

The positiveness check mentioned in a previous section is important for reducing numerical diffusion and ensuring the conservation law. For both the pre-growth and post-growth linear methods, the distribution function should be modified according to (3.5) when the positiveness is violated. Note that (3.5) is formulated in such a way that (3.8) is still valid for the new distribution function so that when $\delta x > 0$,

$$\Delta N = 0, \quad \Delta M = 0, \quad \text{for } x_+ < x_2$$

$$\Delta N = \mathcal{N}(0, x_+, k_x, x_2, x_2'), \quad \Delta M = \mathcal{N}(0, x_+, k_x, x_2, x_2''), \quad \text{for } n(x_1) < 0 \quad (3.11)$$

$$\Delta N = \mathcal{N}(0, x_+, k_x, x_2, x_1), \quad \Delta M = \mathcal{N}(0, x_+, k_x, x_2, x_1), \quad \text{for } n(x_2) < 0$$

and when $\delta x < 0$,

$$\Delta N = 0, \quad \Delta M = 0, \quad \text{for } x_+ > x_1$$

$$\Delta N = \mathcal{N}(0, x_+, k_x, x_1, x_1), \quad \Delta M = \mathcal{N}(0, x_+, k_x, x_1, x_1), \quad \text{for } n(x_1) < 0 \quad (3.12)$$

$$\Delta N = \mathcal{N}(0, x_+, k_x, x_1', x_1), \quad \Delta M = \mathcal{N}(0, x_+, k_x, x_1', x_1), \quad \text{for } n(x_2) < 0$$

With the positiveness check, particle transfer is not always performed in each time step. The new distribution may be still within the range of the original bin limits, as shown in the diagram below.

![Diagram](image-url)

Figure 3.7: Example of when there should be no particle transfer because of the incomplete distribution. The white area is the original distribution and the shaded area denotes the new distribution.
3.1.3.4. **Nonlinearity Adjustment**

The major assumption applied in the hybrid bin method is that the number density distribution within a bin is linear. For the pre-growth linear method, it is also assumed that the distribution maintains its linearity during growth. Let us take the condensational growth as an example to see how reasonable such assumptions are. The condensational growth rate can be expressed in various forms:

\[
\frac{dr}{dt} \cong \frac{B \Delta S}{r}, \text{ or }
\]

\[
\frac{dm}{dt} \cong (4\sqrt{3} \pi \rho_w)^{2/3} B \Delta S m^{1/3}, \text{ or (3.13)}
\]

\[
\frac{d(r^2)}{dt} \cong 2 B \Delta S,
\]

where \(r\) is the particle radius, \(B\) is an environmental growth parameter, \(\rho_w\) is the density of water, and \(\Delta S\) is the excess of the environmental saturation ratio over the drop saturation ratio. The detail of the parameter \(B\) can be found in Section 3.2.3, and has typical values of \(\sim 6 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}\) at \(0^\circ\text{C}, 1000 \text{ mb}\); \(3 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}\) at \(-20^\circ\text{C}, 500 \text{ mb}\). Each of the first two forms of the rate equation is nonlinear with respect to radius and mass, respectively. However, the last form shows that the growth of particle surface area \((\propto r^2)\) is independent on neither radius nor mass. Figure 3.7 shows that the distribution function can indeed maintain its linearity only on an \(r^2\)-coordinate. The commonly used logarithmic coordinate (\(\log r\) or \(\log m\)) is most vulnerable to errors caused by the non-linearity, while the \(r^2\)-coordinate scheme exhibits perfect linearity for condensational growth.
Figure 3.8: Non-linearity for bin-shift in log-$r$, linear-$r$, and $r^2$ coordinates. For an initially linear distribution, the bin-shift due to condensation growth is linear only in the $r^2$ coordinate.
The error associated with the assumption of a linear-distribution is usually small for a growth that is small relative to the bin sizes but can be quite significant in fast growing situations. For a 0.5% environmental supersaturation, the growth rate of a 10 \( \mu m \) drop is about 0.05 \( \mu m \) s\(^{-1}\), but it is 0.5 \( \mu m \) s\(^{-1}\) for a 1 \( \mu m \) drop. In a logarithmic scale, the condensational growth rate is large with respect to the bin-size for smaller drops \( \frac{d\ln m}{dt} \propto m^{2/3} \). So, the error caused by the assumption of linear-distribution is largest for the smallest drops, and during the activation stage. Although some numerical schemes could be used to ensure a small relative growth, the error is still cumulative. It seems that \( r^2 \) would be the best choice as the bin-component variable. However, not all the growth processes share the same non-linearity. Besides, a good bin method should not be restricted to a specific bin-sizing factor. Using the post-growth linear scheme can avoid the problem of non-linear bin-shift. The problem left is now: whether the growth of the mean can adequately represent the mean growth -- an assumption made in the first part of the hybrid bin-method (the semi-discrete growth). We will have some detailed discussion on this problem next.

The mean growth, \( \overline{\delta x} \), and the growth of the mean, \( \delta \overline{x} \), during a time step \( \delta t \) can be derived from equations (3.7) and (3.8) using finite difference calculations:

\[
\overline{\delta x} = \frac{\Delta M}{N} = \delta t \frac{dM}{dt} = \delta t \frac{\int_{x_1}^{x_2} dx}{N} \frac{d}{dt} n(x) dx, \tag{3.14}
\]

\[
\delta \overline{x} = \delta t \left. \frac{dx}{dt} \right|_{x = \overline{x}}. \tag{3.15}
\]

If the growth kernel \( \frac{dx}{dt} \) is of degree-\( A \) such that

\[
\frac{dx}{dt} = C x^A, \tag{3.16}
\]

where \( C \) is a constant, one can derive from (3.14) and (3.15)
\[ \delta \overline{x} = \frac{C \delta t}{N} \int_{x_1}^{x_2} x^A [n_o + k(x-x_o)] \, dx, \quad \text{and} \]

\[ \delta \overline{x} = C \delta t \; \bar{x}^A. \]  

Further defining \( q \equiv x_2 / x_1 \), which is the bin-sizing factor, and \( p \equiv \overline{x} / x_1 \), which is the position of the mean in the bin \( (1 \leq p \leq q) \), we can solve \( \delta \overline{x} \) as

\[ \delta \overline{x} = C \delta t \; \bar{x}^A \xi, \]  

where

\[
\xi = \frac{1}{p^A(q-1)^3} \left\{ \frac{q^{A+1} - 1}{A + 1} (q - 1)^2 - 6(p - \frac{q + 1}{2}) \left[ \frac{q^{A+1} - 1}{A + 1} (q + 1) - \frac{2(q^{A+2} - 1)}{A + 2} \right] \right\},
\]

except for \( A = -1 \), in which case

\[
\xi = \frac{p}{(q-1)^3} \left\{ \ln[(q-1)^2] - 6(p - \frac{q + 1}{2}) \left[ - \ln[q(q + 1)] + 2(q - 1) \right] \right\},
\]

and for \( A = -2 \),

\[
\xi = \frac{p^2}{(q-1)^3} \left\{ -(q^2 - 1)(q - 1)^2 - 6(p - \frac{q + 1}{2}) \left[ -(q^4 - 1)(q + 1) + 2 \ln q \right] \right\}.
\]

The parameter \( \xi \), as shown in Figure 3.8, represents the accuracy of the semi-discrete growth method as a function of \( A, p, \) and \( q \). The growth of the mean, \( \delta \overline{x} \), is exactly the same as the mean growth \( \delta \overline{x} \) \( (\xi = 1) \) for the zeroth- and first-degree kernels \( (A = 0 \text{ and } 1) \). The use of the linear distribution function is less accurate for higher-degree nonlinearities. The growth calculated from the mean best approximates the mean growth when the mean is at about a quarter of the bin-size from either of the bin-limits and is worst when the mean is near the bin-limits. Note that the errors tend to be averaged out while \( p \) varies progressively from 1 to \( q \). The error of approximation \( (\equiv |1-\xi|) \) for a
bin-sizing factor of $q = \sqrt{2}$ is about an order of magnitude smaller than that for $q = 2$. Therefore, the accuracy gained by using smaller bin-sizes can compensate the extra computational time needed for the extra bins.

Recall that the hybrid bin method is not restricted to the use of growth kernels of polynomial form. If such a polynomial does exist, however, we can still utilize $\xi$ as an adjustment factor. For a polynomial growth rate in the form of

$$\frac{dx}{dt} = \sum_j (a_j x^j), \quad (3.20)$$

the modified mean growth can be expressed as

$$\delta \bar{x} = \delta t \sum_j (a_j \bar{x}^j \xi_j), \quad (3.21)$$

where $\xi_j$ is the adjustment factor for $A = j$, and $a_j$ is the coefficient of each term in the polynomial.
Figure 3.9: Adjustment factor $\xi$ for the non-linearity associated with the *semi-discrete growth method*, expressed as a function of the degree of the non-linearity $A$, the bin-sizing factor $q$, and the position of the mean of the component value in the bin $p$. 
3.1.3.5. Multi-grid Bin-shift

One of the disadvantages of the method-of-moments scheme of Tzivion et al. (1987) is that a fixed bin-sizing factor (i.e., a logarithmic categorization) is normally required. Furthermore, a bin-sizing factor of $q = 2$ is almost a necessity because (1) the numerical algorithm becomes quite unmanageable for $q \neq 2$ and (2) it is difficult to deal with a bin-shift over multiple bins (grids). Let us focus on the latter problem here.

Other than producing clean numerical formulas, using $q = 2$ in the method-of-moments limits the particle transfer only to the adjacent bins for hydrodynamic collections since a larger drop can not more than double its original mass by collecting a smaller drop. However, there are many situations in which the distribution needs to be shifted to multiple bin-distances away or even to spread over multiple bins. Take the log $r$ coordinate in Figure 3.7 as an example: the bin that contains evaporating drops tends to stretch (just opposite to the growth situation), in which case a multiple-bin shift would be required. Also, for hydrodynamic interactions, multi-grid shifts are necessary for drops collecting more than one drop at a time, or when a bin-sizing factor of $q < 2$ is used.

The hybrid bin method does not require a fixed bin-sizing factor. Figure 3.10 shows a schematic representation of a multi-grid bin-shift. The magnitude of the number and mass transferred into each bin can be obtained using the notations defined in (3.9):

\[
\begin{align*}
\text{BIN 1:} & \quad \Delta N &= \mathcal{N}(n_0, x_o, k, x_a, x_2), \quad \Delta M = \mathcal{M}(n_0, x_o, k, x_a, x_2), \\
\text{BIN 2:} & \quad \Delta N &= \mathcal{N}(n_0, x_o, k, x_2, x_3), \quad \Delta M = \mathcal{M}(n_0, x_o, k, x_2, x_3), \quad (3.22) \\
\text{BIN 3:} & \quad \Delta N &= \mathcal{N}(n_0, x_o, k, x_3, x_b), \quad \Delta M = \mathcal{M}(n_0, x_o, k, x_3, x_b).
\end{align*}
\]

Note that the bin-sizing factor is not involved in calculating these formulas. This method can be applied to spatial frameworks that normally use linear coordinates. It also allows zero or negative component values, which are not possible in logarithmic coordinates.
The freedom of choosing the desired bin-sizes is potentially valuable. For instance, the activation of cloud drops is important in the size range of $r < 20 \, \mu m$, while the hydrodynamic collection processes require finer resolution at the range of $r > 40 \, \mu m$. It would be advantageous to have the ability to adjust the bin-sizing according to such specific requirements. One may want to have *locally enhanced resolution* (similar to the grid-nesting concept) at several specific locations of the spectrum to capture the essence of a specific process. It is also possible to design a *run-time adjustable* categorization scheme using the hybrid bin method to track a major growth event and thus provide more resolution at where and when it is needed.

![Figure 3.10: Schematic diagram of the multi-grid shift. The distribution was originally in BIN 1 (dashed line). After the growth, it occupies BIN 1, BIN 2, and BIN 3 with new bin limits $x_a$ and $x_b$.](image-url)
3.1.3.6. Multi-Dimensional Bin-Shift

The particle frameworks applied in this study have more than one component. Thus, we will need a scheme for multi-dimensional bin shift since particles could evolve in many components at the same time. For instance, the bin-shift should be performed in both the water and solute axes for coalescence process since large drops accrete both water and solute mass from small drops. Figure 3.11 is a schematic diagram of the multi-dimensional bin shift in the hypothetical components A and B. The original particles in bin (A1,B1) are transferred to bins (A2,B1), (A2,B2), (A3,B1), and (A3,B2). Since all the components are independent of each other, we can consider the bin-shift to be done in two steps: (1) move horizontally along the A-axis, then (2) move up along the B-axis. Each step follows the procedures for a single-component bin-shift, as discussed previously. For step (1), the number and total A-component property being transferred to bin A2, A3 are defined as \( \Delta N_A(2) \), \( \Delta M_A(2) \), and \( \Delta N_A(3) \), \( \Delta M_A(3) \), respectively. These parameters can be converted into the percentage of particles transferred to each bin

\[
P_A(2) = \frac{\Delta N_A(2)}{N}, \quad P_A(3) = \frac{\Delta N_A(3)}{N},
\]

with their mean A-component property expressed as

\[
\bar{x}_A(2) = \frac{\Delta M_A(2)}{N}, \quad \bar{x}_A(3) = \frac{\Delta M_A(3)}{N}.
\]

Likewise, for step (2), we have

\[
P_B(1) = \frac{\Delta N_B(1)}{N}, \quad P_B(2) = \frac{\Delta N_B(2)}{N},
\]

\[
\bar{x}_B(1) = \frac{\Delta M_B(1)}{N}, \quad \bar{x}_B(2) = \frac{\Delta M_B(2)}{N}.
\]

The exact number of particles transferred to bin (A2,B1), (A2,B2), (A3,B1), and (A3,B2) and their mean properties then can be found as
Figure 3.11: Schematic diagram of the multi-dimensional bin-shift in two components. The original distribution is in bin (A1,B1).

\[
\begin{align*}
\Delta N(2,1) &= N P_A(2) P_B(1), \text{ with mean properties } \bar{x}_A(2) \text{ and } \bar{x}_B(1); \\
\Delta N(2,2) &= N P_A(2) P_B(2), \text{ with mean properties } \bar{x}_A(2) \text{ and } \bar{x}_B(2); \\
\Delta N(3,1) &= N P_A(3) P_B(1), \text{ with mean properties } \bar{x}_A(3) \text{ and } \bar{x}_B(1); \\
\Delta N(3,2) &= N P_A(3) P_B(2), \text{ with mean properties } \bar{x}_A(3) \text{ and } \bar{x}_B(2). \quad (3.26)
\end{align*}
\]

This scheme can be generalized for more than two components and for multi-grid shift.

The transfers in individual components are:

\[
\begin{align*}
P_A(i) &= \frac{\Delta N_A(i)}{N}, \quad P_B(j) = \frac{\Delta N_B(j)}{N}, \quad P_C(k) = \frac{\Delta N_C(k)}{N}, \quad \ldots \\
\bar{x}_A(i) &= \frac{\Delta M_A(i)}{N}, \quad \bar{x}_B(j) = \frac{\Delta M_B(j)}{N}, \quad \bar{x}_C(k) = \frac{\Delta M_C(k)}{N}, \quad \ldots \quad (3.27)
\end{align*}
\]

where \(i, j, k, \ldots\) are the bin numbers of component A, B, C, ..., etc. The overall number transferred into each bin is then
\[ \Delta N(i, j, k, ...) = N_P A(i) P_B(j) P_C(k) ..., \quad (3.28) \]

with particle properties of

\[ \bar{x}_A(i), \bar{x}_B(j), \bar{x}_C(k), ..., \text{etc.} \quad (3.29) \]

It can be easily proven that this scheme satisfies the conservation of number and component properties. Note that the multi-dimensional bin-shift method is conceptually similar to the particle-in-cell finite element method proposed by Staniforth and Mitchell (1977) and Bermejo (1990), which was used for multi-dimensional advection problems.

### 3.1.3.7. Bin Components and Particle Properties

#### 1. Bin Components

In cloud modeling, the mass of water is the most commonly used bin-component because it is normally the major constituent of cloud particles. In order to study the cloud chemistry, however, we must include solute as the second bin-component. Among many constituents of the solute mixture, only the major chemicals are chosen as this second bin-component. Sulfate is normally the major solute components for both the continental and maritime clouds, although one might want to include sodium-chloride as a second solute component in some maritime situations. The hybrid bin-methods works the same way for solute mass as it is for water mass. Furthermore, it can also be applied to particle properties other than mass. Table 3.1 is a list of the possible candidates for the particle bin-component and their corresponding bin variable, number density function, and the zeroth and first moments.
Table 3.1: Various bin-components and the sub-bin distribution functions. **A**: particle frameworks; **B**: spatial frameworks (for the spatial distribution of temperature $T(x)$ and pressure $P(x)$).

### A: Particle framework:

<table>
<thead>
<tr>
<th>parameter</th>
<th>bin variable $x$</th>
<th>distribution function $n(x)$</th>
<th>zeroth moment $N = \int n(m) , dm$</th>
<th>first moment $M = \int m , n(m) , dm$</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass</td>
<td>$M$</td>
<td>$n(m)$</td>
<td>$\int n(m) , dm$</td>
<td>$\int m , n(m) , dm$</td>
</tr>
<tr>
<td>radius</td>
<td>$R$</td>
<td>$n(r)$</td>
<td>$\int n(r) , dr$</td>
<td>$\int r , n(r) , dr$</td>
</tr>
<tr>
<td>volume</td>
<td>$V$</td>
<td>$n(v)$</td>
<td>$\int n(v) , dv$</td>
<td>$\int v , n(v) , dv$</td>
</tr>
<tr>
<td>surface area</td>
<td>$A$</td>
<td>$n(A)$</td>
<td>$\int n(A) , dA$</td>
<td>$\int A , n(A) , dA$</td>
</tr>
<tr>
<td>aspect ratio</td>
<td>$\phi$</td>
<td>$n(\phi)$</td>
<td>$\int n(\phi) , d\phi$</td>
<td>$\int \phi , n(\phi) , d\phi$</td>
</tr>
<tr>
<td>height</td>
<td>$H$</td>
<td>$n(h)$</td>
<td>$\int n(h) , dh$</td>
<td>$\int h , n(h) , dh$</td>
</tr>
<tr>
<td>distance</td>
<td>$X$</td>
<td>$n(x)$</td>
<td>$\int n(x) , dx$</td>
<td>$\int x , n(x) , dx$</td>
</tr>
</tbody>
</table>

### B: Spatial framework analogies:

<table>
<thead>
<tr>
<th>distance, height</th>
<th>$X$</th>
<th>$T(x)$</th>
<th>$N = \int T(x) , dx$</th>
<th>$M = \int x , T(x) , dx$</th>
</tr>
</thead>
<tbody>
<tr>
<td>distance, height</td>
<td>$X$</td>
<td>$P(x)$</td>
<td>$N = \int P(x) , dx$</td>
<td>$M = \int x , P(x) , dx$</td>
</tr>
</tbody>
</table>
The first four parameters in the table are closely related for liquid-phase particles since cloud droplets can normally be considered as spherical and have constant density. Even for large drops that are not quite spherical, their eccentricity can generally be retrieved from the knowledge of the drop mass. For ice-phase particles, however, these parameters are explicitly independent. Extra parameters must be used in order to properly describe ice particles and their growth processes. The aspect ratio $\phi$ defined in Section 2.3.1 is a parameter frequently used to describe the shape of ice crystals. Because of the availability of the theoretical and experimental information, the aspect ratio $\phi$ is chosen as the third bin-component for ice particles.

The definition of the aspect ratio, $\phi \equiv \frac{c}{a}$, gives large values to columnar ice (elongated along the crystallographic $c$ axis) and small values to planar ice (elongated along the $a$ axis). The use of a linear $\phi$ axis is thus biased toward the $c$-axis of the ice crystals. It is more reasonable to use $\log \phi$ instead, so that $\log \phi > 0$ for columnar ice and $\log \phi < 0$ for planar ice. A good physical reason of doing this is that the change of $\phi$ due to either diffusional or accretional growth is log-linear (see Section 2.3.2 and 2.3.3). On a $\log \phi$ axis, the bin-shift is perfectly linear and the computation for the bin methods is fast with minimal error.

The density of ice particles, defined as mass divide by the circumscribed volume (including the void space), does not vary as much in magnitude (normally between 0.1 to 0.91 g cm$^{-3}$) as does the mass and aspect ratio of ice crystals. Therefore, it is not essential to include density as a bin-component at this point. The volume and size of ice crystals can normally be retrieved from their mass and density and hence are not selected as a bin-component either. The total surface area is probably the most complicated physical property of ice particles. Ice particles may branch or become hollow during diffusional growth, and become spongy during riming. Knowing mass and density, we can only derive the "circumscribed surface area" but never the actual total surface area.
This total surface area controls the diffusional growth of ice particles. Because the total surface area is a reflection of the branching and hollowness, ice crystals of the same mass, size, and aspect ratio may still behave differently because of different surface areas. Total surface area is not only important to the microphysical processes, but also to the adsorption of trace chemicals. However, due to insufficient knowledge, the total surface area can not be included as a particle property at this stage, needless to say as a bin-component.

As listed in Table 3.1, "height" can also be a particle property. In fact, all the three spatial dimensions should be included in the particle frameworks since each particle has a specific position in the atmosphere. Particles can have a sub-grid distribution within a spatial bin just as it has in a mass bin. Without the spatial components, numerical diffusion in space is deemed to occur for advection type problems. One special implementation of the spatial components is the gravitational advection (sedimentation) of particles. Without resolving the sub-grid particle distribution, precipitation may propagate downward too fast due to numerical diffusion. The grid arrangement of the spatial bin-components can be done in the same way as the spatial framework. Each group of particles has a height/distance variable that has a value within the range of its spatial bin-limits.

As mentioned earlier, the bin-method can also be applied to a spatial framework for dynamic calculations. Distinction must be made, however, between the spatial framework and the spatial-components of the particle framework. The spatial distribution of air temperature or pressure in space is the parameter of concern in the former while the distribution of particle number concentration in various components is the theme of the latter. The last two entries in Table 3.1 show the spatial framework analogies for the temperature and pressure distribution functions. Although different in
physical concept, we can see that the two types of framework are mathematically the same.

2. Particle Properties

Besides the main grouping parameter, the total number concentration, several physical and chemical properties are necessary to describe the particles in each bin. The major ones are the component parameters -- water mass, solute mass, aspect ratio, and height/distance. Before mentioning the other properties, it should be pointed out that extensive properties are more useful than the intensive properties because the extensive properties can be used directly for advection- and diffusion-type calculations. Therefore, drop mass is superior to drop size, and volume is preferred to density. Some intensive properties can be converted to extensive properties by multiplying by the particle mass or, in some cases, the total number density. For example, the mean temperature multiplied by the total mass will result in a new variable that is analogous to the total heat. Height times the total mass, then, represents the gravitational potential energy. However, it is difficult to interpret what is the extensive property of the aspect ratio. In this study, log $\phi$ multiplied by the number density or the total mass is used.

Among the aforementioned parameters, temperature, height, and aspect ratio are the physical or thermodynamic properties while water mass and the major solute mass are considered as the chemical properties. For the simulation of cloud chemistry, we can also include other chemical properties -- the minor solute constituents. Table 3.2 is a summary of the various bin-components and particle properties for the particle framework used in this study.
Table 3.2: List of the bin components and particle properties in the gas-phase and the liquid- and ice-phase particle frameworks. Note: $y_j$ denotes the total moles of $j$ in either the gas or the condensed phase per mole of air.

<table>
<thead>
<tr>
<th>GAS-PHASE</th>
<th>LIQUID-PHASE</th>
<th>ICE-PHASE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>bin components</strong></td>
<td><strong>GROUPING PARAMETER</strong></td>
<td><strong>GROUPING PARAMETER</strong></td>
</tr>
<tr>
<td>H: space</td>
<td>N: total number density</td>
<td>N: total number density</td>
</tr>
<tr>
<td>W: water mass</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S: solute mass</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H: space</td>
<td></td>
<td></td>
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3.1.4. Test and Discussion

Before going into a full implementation of the concepts discussed so far, we shall test the hybrid bin method on some idealized cases and compare the results with existing analytical solutions to check the computational integrity and efficiency. An additional test will be presented to show how well the hybrid bin method works with realistic growth kernels. Following the tests, discussion on a particular problem with the hydrodynamic collections will be presented.

3.1.4.1 Comparison with the Analytical Solutions

1. Condensation/evaporation

The test of the hybrid bin-method is first carried out on the growth of droplets by vapor diffusion. Let us consider the growth equation for relatively large and highly diluted droplets:

\[
\frac{dm}{dt} = m^{1/3} B s, \quad (3.30)
\]

where \( B \) is a function of temperature and pressure and \( s \) is the supersaturation. Tzivion et al. (1989) gave an analytical solution for the drop number distribution as a function of time, mass, and the original number density function at \( t = 0 \):

\[
n(m,t) = m^{1/3} \left[ m^{2/3} - \frac{2}{3} \alpha \right]^{1/2} n \left( \left[ m^{2/3} - \frac{2}{3} \alpha \right]^{3/2}, 0 \right), \quad (3.31)
\]

where \( \alpha = \int_0^t B s \, dt \) is a function of time. For the diffusional mass transfer, evaporation rates can be many orders of magnitude greater than the condensation rate due to the possibility of large undersaturation \((s < 0)\). Normally, the evaporation process requires smaller time steps and causes more numerical problems than condensation. We will do
the test on the more extreme case by allowing a population of droplets to evaporate in an environment of 70% humidity \((s = -0.3)\). Under standard temperature and pressure, \(\alpha\) equals \(B st\), and \(B\) is about \(-6 \times 10^{-7}\) mol\(^{2/3}\) s\(^{-1}\). Let us consider the evolution of a commonly used, non-dimensional drop number density function from Berry (1967):

\[
F(X,0) = 4X \exp(-2X), \tag{3.32}
\]

where \(X = m/m_o\) is the mass normalized to the mode of the distribution \(m_o\). The initial distribution function in terms of the actual mass is

\[
n(m,0) = \frac{N_o}{m_o} F(X,0) = \frac{4 N_o}{m_o^2} m \exp\left(-2 \frac{m}{m_o}\right), \tag{3.33}
\]

where \(N_o = 239\) cm\(^{-3}\) is the total number density, and \(m_o = 2.8 \times 10^{-4}\) g (equivalent to a radius of 400 \(\mu\)m) is the mode of the distribution. The analytical solution for the number distribution can then be derived as

\[
n(m,t) = \frac{4 N_o}{m_o^2} m^{1/3} \left[ m^{2/3} - \frac{2}{3} \alpha \right]^2 \exp\left[-\frac{2}{m_o} \left(m^{2/3} - \frac{2}{3} \alpha\right)^{3/2}\right]. \tag{3.34}
\]

The accuracy of the simulated results, as shown in Figure 3.12, is similar to that of Tzivion et al. (1989), who did a comparable comparison using the method-of-moments. The hybrid bin method is fairly accurate for the condensation/evaporation equation even with a time step as large as 100 seconds. The accuracy does not improve much with smaller time steps but does improve with a smaller bin sizing factor. Improvement is also achieved when the \textit{adjustment factor} (3.19) is used.
Figure 3.12: Comparisons of the results from the hybrid bin-method with an analytical solution for the evolution of drop number distribution due to evaporation. The air humidity is fixed at 70%. The result shown is after 50 min of simulation time. The top axis is the drop radius, the bottom axis is the bin number, and the vertical axis is the number of particles in each bin normalized to the total number.
2. Coalescence with Constant Kernel

The hybrid bin method is also tested for the growth of droplets by coalescence. The time dependent stochastic coalescence equation can be written in the form of

$$\frac{\partial n(x,t)}{\partial t} = \frac{1}{2} \int_0^\infty n(x-y)n(y,t)K(x-y,y)dy - n(x,t)\int_0^\infty n(y,t)K(x,y)dy,$$

(3.35)

where $K(x,y)$ is the kernel for a drop with mass $x$ to collect a drop that has mass $y$. The actual collection kernel is a very complicated function. For comparison purpose, some idealized collection kernels are used so that analytical solutions are available. We shall use a constant kernel $K_o$ in the first test. The drop distribution function used is the same as that in the previous test but with a mode $m_o = 4.18 \times 10^{-9}$ g (equivalent to 10 µm in radius) to represent a cloud drop population. Defining a dimensionless time variable $T = K_o N_o t$, Bleck (1970) gave the analytical solution of drop spectrum as a function of time:

$$F(X,T) = \frac{8e^{-2X} \sinh \left[ 2X \left( \frac{T}{T + 2} \right)^{1/2} \right]}{T^{1/2} \left( T + 2 \right)^{3/2}}.$$  (3.36)

Figure 3.13 shows the results for a constant kernel of $K_o = 1.8 \times 10^{-4}$ cm$^3$ s$^{-1}$ and a liquid water content ($=N_o m_o$) of 1 g m$^{-3}$. The results from the hybrid bin-method follow very closely with the analytical solutions and the accuracy is similar to that in Tzivion et al. (1987), who used the method-of-moments. Note that the result in their Figure 1 is actually a simulation after only 6 minute simulation time instead of the 60 minutes as indicated. Several time steps are used in this comparison. The results are similar for time steps of 1, 3, and 10 seconds. A noticeable deviation is observed, however, in the result using a 30 second time step. The error associated with the large time-step is partly due to an "over-depletion" problem, which will be explained in Section 3.3.3.
Figure 3.13: Comparison of the stochastic collection computations for a constant kernel of $K_0 = 1.8 \times 10^{-4}$ cm$^3$ s$^{-1}$. The spectra are for 0, 10, 20, 40, and 60 min simulation times. The horizontal axes are the same as the previous figure. The vertical axis is now the fractional mass. The analytical solutions are represented by the dashed lines and the hybrid bin method by the solid lines.
3. Coalescence for Golovin's Kernel

From the discussion in Section 3.1.3.4, it is expected that the hybrid method works well on the constant growth kernel. A more rigorous test is performed here against the nonlinear Golovin's kernel $K(x,y) = b(x + y)$, where $b$ is a constant. This kernel is somewhat more realistic than the constant kernel because of the drop mass dependence. With the same distribution function as used previously, the analytical solution of the drop distribution function for Golovin's kernel is (Bleck, 1970)

$$F(X, \tau) = (1 - \tau)e^{-\tau X/L} \sum_{k=0}^{\infty} \frac{\tau^k X^{2k+1}}{(k+1)! (2k+1)!},$$  \hspace{1cm} (3.37)

where $\tau = 1 - e^{-T}$, and $T \equiv b N_0 m_0 t$. However, the summation term is not easy to compute, especially for large $X$ values. Tzivion et al. (1987) referenced this analytical solution. However, judging from their results, the distribution function they used must have been the exponential distribution function that was used by Berry (1967):

$$g(lnr) = 3 N_0 m_0 X^2 \exp(-X).$$  \hspace{1cm} (3.38)

It is a mass distribution which can be converted to the number density function

$$n(m,0) = \frac{N_0}{m_0} \exp\left(-\frac{m}{m_0}\right).$$  \hspace{1cm} (3.39)

We shall use this distribution function instead in order to compare with results presented by Tzivion et al. (1987). The time-dependent distribution function has an asymptotic approximation of:

$$n(m,t) = \frac{L}{\sqrt{2\pi}} \frac{X^{1/2}}{m^{1/2}} \exp\left[-(\tau^{1/2} - 1)^2 X - Lbt\right],$$  \hspace{1cm} (3.40)
where $L = N_o m_o$ is the liquid water content, $X = m / m_o$, $\tau = 1 - \exp(-Lbt)$, and $b$ is the constant coefficient in the Golovin's kernel. Figure 3.14 demonstrates the evolution of the drop spectrum after 30 and 50 minutes for $b = 1530 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$. The top diagram shows that the results from the hybrid bin method, although better than the Bleck's solution (see Figure 2a of Tzivion et al., 1987), it is not very satisfactory. Such discrepancy is mainly caused by the non-linearity introduced by the Golovin's kernel.

Another source of error is quite interesting and will be discussed in the next section. Significant improvement can be obtained, as shown in the bottom diagram, when a smaller bin sizing factor of $\sqrt{2}$ is used. Note that the asymptotic approximation is not accurate for smaller drop sizes. Therefore, the error at 30 min is actually smaller than it appeared to be.
Figure 3.14: Same as Figure 3.13 but for Golovin's kernel. The bin sizing factor used for the top and bottom graphs are 2 and $\sqrt{2}$, respectively.
4. **Tri-model Drop Size Distribution**

An extended test is done here applying realistic coalescence kernels as well as the breakup scheme discussed in Section 2.2.3.2. This test is designed with added interest on the details of the raindrop size distribution. A conventional parameterization for the raindrop size spectrum used in bulk-water cloud models assumes the empirically obtained Marshall-Palmer type distribution (Marshall and Palmer, 1948):

\[
n(d) = N_0 \exp(-\Lambda d), \tag{3.41}
\]

where \(d\) denotes drop diameter (mm), \(N_0 = 8 \times 10^{-6} \text{ mm}^{-4}\), and \(\Lambda\) is the slope of the log-linear distribution function, which can be determined from the rainfall rate. This exponential function is only a first-order approximation, which was determined empirically from averaged observational data. Using the detailed spectral (bin) method and the realistic coalescence and breakup schemes, we are able to discover some detailed features of a more realistic raindrop size distribution. The test is done by assuming an initial Marshall-Palmer distribution for the raindrops. The raindrop spectrum is then allowed to evolve by coalescence and breakup, as shown in Figure 3.15. The evolution of the drop spectrum starts with the breakup of large drops and the creation of submillimeter-sized small drops. While the number of large drops decreases continuously, the number of small drops oscillates toward an equilibrium value. The whole spectrum becomes quite stable after about 30 min and evolves into a tri-modal distribution. This result is in good agreement with the numerical simulations of List et al. (1987) and Brown (1988; 1989). Note that a fair comparison cannot be made to the results published before 1987 (e.g., Valdez and Young, 1985; Brown, 1987) due to a correction (List et al., 1987) of the breakup formulas by the original authors.
Figure 3.15: Tri-modal drop-size spectrum evolved from an initial Marshall-Palmer type distribution (dashed-line) with realistic coalescence kernel and breakup scheme. The bottom graph is a partial enlargement of the top graph. The density of the curves indicates the time of simulation, with 10 min increment for each level of line density. The darkest line shows the drop size spectrum at 50 min of simulation time.
Tri-modal size distributions, such as those shown in Figure 3.15, seem to be supported by the observational results of Steiner and Waldvogel (1987) as well as those of Zawadzki and de Agostinho Antonio (1988). Normally, a disdrometer is used to measure the raindrop size distribution. However, Sheppard (1990) found that the disdrometer has irregularities in the size classifications leading to artificial peaks, and the multi-modes is actually less obvious. Some numerical simulations also showed that such tri-modal distribution might not exist. The simulation of Tzivion et al. (1989) showed that the tri-modal feature diminishes gradually when there is substantial evaporation. Chen and Lamb (1992a, Figure 7) also showed that the tri-modal feature is not obvious when the raindrop spectrum is evolved from a continuous collection of cloud drops. It seems that the tri-modal equilibrium is hard to reach when there is a continuous sink (evaporation) or source (supply of cloud drops). The time needed for the Marshall-Palmer spectrum to reach the equilibrium tri-modal distribution is around 15 min to 1 hour in various similar simulations. Such long time constants might explain why the tri-modal distribution does not always exist. Nevertheless, the traditional Marshall-Palmer type assumption is correct only to a first-order. Large errors could be introduced by such first-order approximation in a non-linear system.

A good example of error caused by the Marshall-Palmer type assumption is the estimation of liquid water contents and rainfall rates from radar reflectivities. The initial (Marshall-Palmer) and the resulting raindrop size distributions in Figure 3.15 have the same rain-water content of $L = 4.7 \text{ g m}^{-3}$. However, the radar reflectivity factor $Z$ is proportional to $d^6$. The initial Marshall-Palmer distribution gives $Z = 2.6 \times 10^5 \text{ mm}^6 \text{ m}^{-3}$ (54 dBZ) while the final tri-modal distribution gives $Z = 7.9 \times 10^4 \text{ mm}^6 \text{ m}^{-3}$ (49 dBZ). The relationship between $Z$ and $L$ that derive from the Marshall-Palmer type assumption can be found in Wisner et al. (1972):
Using the actual radar reflectivity from the tri-modal distribution to estimate the rainwater content, however, one would get $L = 2.18 \, \text{g m}^{-3}$, which gives an underestimation of more than 50%. A commonly used $Z$-$R$ relationship derived from the Marshall-Palmer type assumption is expressed as (Doviak and Zrnić, 1984, p. 201)

$$Z = 200 \, R^{1.6},$$

which gives a rainfall rate $R$ of 88 mm hr$^{-1}$ from the Marshall-Palmer distribution and 42 mm hr$^{-1}$ from the tri-modal distribution. From the above analyses, one can see the importance of knowing the actual raindrop size as opposed to the Marshall-Palmer type assumption. Another point worth mentioning is that using spectral models, one can actually calculate the radar reflectivity factor from the detailed models and compare it with those from field measurements. Such direct comparisons can be a valuable tool for the verification of results from both the numerical modeling and field measurements.

### 3.1.4.2. Problems on the Coalescence Growth: The Trapezoidal Distribution

The hybrid bin method assumes a linear distribution for particles in a bin either before or after the growth. The error associated with such assumption has been discussed in Section 3.1.3.4. However, the non-linearity problem for the coalescence growth is complicated by the fact that there are two distribution functions involved. Let us assume that the two distribution functions for the drops involved in the coalescence are:

$$n_x(x) = a_x + k_x \, x,$$

$$n_y(y) = a_y + k_y \, y,$$

which gives a rainfall rate $R$ of 88 mm hr$^{-1}$ from the Marshall-Palmer distribution and 42 mm hr$^{-1}$ from the tri-modal distribution. From the above analyses, one can see the importance of knowing the actual raindrop size as opposed to the Marshall-Palmer type assumption. Another point worth mentioning is that using spectral models, one can actually calculate the radar reflectivity factor from the detailed models and compare it with those from field measurements. Such direct comparisons can be a valuable tool for the verification of results from both the numerical modeling and field measurements.

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where \( a_x \) and \( a_y \) are constant, \( k_x \) and \( k_y \) are the slopes, and subscripts \( x \) and \( y \) are the bin variables for the smaller drops and the larger drops, respectively.

As shown in Figure 3.16, we let the bin limits for the collector drops be \( y_1 \) and \( y_2 \), and the limits for the collected drops be \( x_1 \) and \( x_2 \). Also, let \( z \) be the bin variable for the distribution of the coalesced drops, which has a lower limit of \( z_1 = y_1 + x_1 \) and an upper limit of \( z_2 = y_2 + x_2 \). The number density in the new bin is not a smooth function of \( z \), but can subdivided into three contiguous sections. The \( z \) range of section \( a \) starts from \( z_1 \) to \( y_1 + x_2 \), followed by section \( b \) to \( y_2 + x_1 \), and then section \( c \) to \( z_2 \).

In section \( a \), the number density at \( z_1 \) is zero since it can be formed only by the combination of one "point" in each bin (point \( x_1 \) and \( y_1 \)). As \( z \) becomes larger, more combinations are available so that the number density increases gradually. In section \( b \), each point can be a combination of all points in either parent bins. The distribution in section \( c \) is similar to that in section \( a \) but with an opposite trend. The total number of drops within a finite width \( \Delta z \) can be expressed as

\[
\Delta N_a = \Delta t \int_{z_1}^{z_2} \int_{y_1}^{y_2} K(x, y)n_x(x)n_y(y)dydx,
\]

\[
\Delta N_b = \Delta t \int_{z_1}^{z_2} \int_{y_1}^{y_2} K(x, y)n_x(x)n_y(y)dydx,
\]

\[
\Delta N_c = \Delta t \int_{z_1}^{z_2} \int_{y_1}^{y_2} K(x, y)n_x(x)n_y(y)dydx,
\]

where the subscripts \( a, b, \) and \( c \) denote the three sections in Figure 3.16. The number density function in each section can then be derived by letting

\[
n_i(z) = \frac{\Delta N_i}{\Delta z} \bigg|_{\Delta z \to 0}.
\]

We will first investigate the constant kernel case and let \( K' = \Delta t K_0 \). From the above equations, the number density functions can be derived as:
Figure 3.16: Schematic diagram of the collectional interaction between drops in two bins and the resulting drop distribution. The top graph is for interaction between two zeroth-order distributions, while the bottom graph is for interaction between two first-order distributions. The shaded areas represent the portion of particles that participate in the coalescence process.
where \( N_x \) and \( M_x \) are the total number and mass in bin \( x \). Note that the distribution in section \( b \) is linear (with respect to \( z \)), while that in section \( a \) and \( c \) is cubic. The shape of the new distribution is more nearly trapezoidal instead of linear. If the original distribution is of zeroth-order, as assumed in Ochs and Yao (1978), the new distribution in section \( a \) and \( c \) would be linear as shown in the upper part of Figure 3.16. When the collected drops are much smaller than the collector drops (\( x \ll y \)), section \( b \) is the dominant part and can be approximated very well with the linear distribution function, as shown by the dashed line. Even when \( x \) is close to \( y \), the area (total number) that will be shifted to the next bin can still be approximated by the hybrid bin-method. However, when the collection kernel is not constant (e.g., the Golovin's kernel), all sections are not linear. This peculiar non-linearity may cause large errors in the hybrid bin-method. Yet, since the variation of the collection kernel \( K(x,y) \) is small for a narrow range of \( x \) and \( y \), one can expect the error to decrease when a smaller bin-sizing factor is used. The effect of the bin resolution on the nonlinearity was demonstrated previously, as shown in Figure 3.14. Note that when a bin-sizing factor \( < 2 \) is used, the multi-grid shift scheme must be implemented.

The peculiar non-linearity associated with the coalescence growth causes problems in the hybrid bin-method. A generalized form of equation (3.47) for non-linear collection kernels can be derived to give analytical solutions for the actual distribution function. Note that the method-of-moments scheme used by Tzivion et al. (1987)
actually included such three-part integration. However, the formulas for such schemes are complicated and require separate integration in each of the three sections for bin-shift. Using smaller bin-sizing factors will reduce the nonlinearity, but cost more computational time. In the present study, the smaller bin-sizing factor is chosen primarily for its simplicity. Also, with the knowledge of the natural microphysical processes, we can eliminate some of the unnecessary fine-resolution. For instance, it is well known that coalescence is weak for drops with sizes below the Hocking limit (~18 µm in radius) and becomes progressively important as the drop-size increases. We can, thus, use a variable bin-sizing factor to have higher resolution toward larger drop sizes and lower resolution for the smaller-size bins. Such arrangement is possible owing to the flexibility of the hybrid bin-method.
3.1.4.3. **Summary**

The *method-of-moments* technique is a state-of-the-art technique for the calculation of the collision coalescence/breakup equations. However, it lacks flexibility and simplicity. A fixed bin-sizing factor of 2 is generally required. The strength of the *method-of-moments* lies in its ability to deal with high-order polynomial collection kernels. However, realistic collection kernels are normally not in polynomial forms (except when one employs a polynomial approximation). For instance, the growth kernel in the collisional coalescence/breakup equation involves the difference of fall velocities, the sweepout cross-section, the collision efficiency, and the coalescence/breakup coefficients. It is not easy even to derive a functional form for each of these parameters, not to mention a generalized polynomial kernel. Note that one can utilize the lookup table technique that will be discussed in Section 3.7.1 to generate a collection kernel of order-one or higher for each pair of bins. However, since the uncertainties in the existing theoretical and experimental collection kernels are quite large, it is not practicable to apply even a first-order collection kernel at this stage. It is better-off to simply use a constant kernel for each pair of parent bins, as long as the uncertainties in the growth kernels are larger than their variation within each bin range. Due to the simplicity and flexibility it can provide, the hybrid bin method is preferred to the *method-of-moments* for the collision coalescence/breakup problems in this study. For processes that do not involve the interaction of two drops, there is the *adjustment factor* that can reduce the error caused by a non-linear growth kernel.

The *method-of-moments* is computationally more efficient than earlier numerical schemes in solving the drop collection problem. For the constant kernel case, the *method-of-moments* of Tzivion et al. (1987) takes 3.0 sec CPU time for a 50-minute (300-step) simulation on the Tel Aviv University CDC 7600 computer. It takes the
hybrid bin-method 0.8 sec for the same calculation on the IBM ES3090-600S mainframe of the Pennsylvania State University. Although a comparison on the same computer is not available, it can be seen from the above figures that the efficiencies of these two methods are at least of comparable magnitude. For the Golovin's kernel case, the computational time increased by more than 50% using the method-of-moment. Yet, the computational time for the hybrid bin-method is not determined by the complexity of the growth kernels, so the computational time required is essentially the same. However, the hybrid bin-method does need a smaller bin-sizing factor. For a doubling of the number of bins, the computation time would increase about four fold. The time step required for the hybrid bin-method can be more than 10 seconds for either the condensation/evaporation or the coalescence/breakup processes, at least in the idealized cases. Such time steps are sufficiently large so that the hybrid bin method does not become the bottleneck of the model calculation.

The most advantageous feature the hybrid bin-method has over the method-of-moments is probably the freedom of selecting bin sizes. It can be applied to practically any bin-sizing schemes for both the particle frameworks and the spatial frameworks. Therefore, besides the vapor diffusional growth and the hydrodynamic interactions, the hybrid bin-method is also applied to the calculation of the height changes of particles due to sedimentation and to the change in solute mass due to chemical reactions.
3.2. Numerical Methods for Diffusional Growth

The time constant for condensational growth was shown in Section 2.4.1 to be proportional to the square of the drop size. Since the drop size may vary by several orders of magnitude during the growth, there exists a great difficulty in determining adequate time steps for numerical integration. As a result, most numerical methods used for the calculation of condensation and evaporation processes require very small time steps. Another common difficulty for the simulation of the condensation/evaporation processes is that a large number of equations need to be solved simultaneously. For each particle category, there is a set of equations for each growth process. These equation sets are inter-connected through their common dependence on the gas-phase parameters. The total number of equations for a sizable particle framework can be too large for differential-equation solvers such as the matrix type methods. It is thus necessary to design special numerical methods for the diffusional growth problem.

Clark (1973) used a semi-analytical method to calculate a time-averaged saturation ratio $S$ during one time step. The growth equations for each drop category can then be calculated independently using this mean saturation ratio. This method avoids the problem of numerical instability associated with the time scale of $S$ but requires very small time-steps during the activation stage. Explicit methods such as the fourth-order Runge-Kutta method employed by Fitzgerald (1974) require a time step of about 0.01 s to ensure stability for the activation of drops. Hall (1980) calculated the average saturation ratio from the initial value and the end results during one time step then used that value to iterate the calculation. Such a method cannot provide good accuracy and stability without using very small time steps for the activation or fast evaporation of drops. Special numerical methods that can help to improve the computational efficiency are thus introduced here.
3.2.1. Quasi-Analytical Solution for the Environmental Saturation Ratio

The rate of change of saturation ratio $S$ in the air can be expressed by the saturation development equation (c.f., equation 13-29 in Pruppacher and Klett, 1978, p. 422)

$$\frac{dS}{dt} = A_1 W - A_2 \frac{dy_w}{dt}. \quad (3.48)$$

Here, $W$ is the updraft speed, $y_w$ is the molar mixing ratio of the condensed water in the air, and

$$A_1 = S \left( \frac{l_v}{c_p T} - 1 \right) \frac{M_a g}{RT} \quad \text{and} \quad A_2 = S \frac{l_v^2}{c_p R T^2} + \frac{P_{air}}{e_s} \quad (3.49)$$

where $c_p$ is the molar heat capacity of air at constant pressure, $M_a$ the molecular weight of air, $g$ the gravitational acceleration, and $e_s$ the saturation vapor pressure over liquid water at temperature $T$. The rate of change of $y_w$ is a summation of the growth rates of each cloud particle of category $i$:

$$\frac{dy_w}{dt} = \sum_i \frac{dm_i}{dt} N_i = \sum_i C r_i (S - S_{r,i}) N_i, \quad (3.50)$$

where the $m_i$ are the water masses of the particles in moles, $N$ the total number of particles per mole of air, $C$ an environmental parameter, and $S_r$ the saturation ratio over drop of radius $r$. Note that for ice particles, $S_r \approx 1$. We can rearrange the above equation into a form similar to that used by Clark (1973):

$$\frac{dy_w}{dt} = aS + b, \quad (3.51)$$

where $a = C \sum_i r_i N_i$ and $b = C \sum_i r_i S_{r,i} N_i$. By assuming $S \approx 1$ in clouds and letting $A_1$, $A_2$, $a$, and $b$ be constant, Clark solved the saturation development equation in the form
\[
\frac{dS}{dt} = A_1 W - A_2 (aS + b) \tag{3.52}
\]

analytically to give the saturation ratio as a function of the initial saturation ratio \(S_o\) after a time interval \(\Delta t\):

\[
S_1 = (S_o - S_{eq}) \exp(-\Delta t / \tau) + S_{eq}, \tag{3.53}
\]

where \(S_{eq}\) is the steady state saturation ratio

\[
S_{eq} = \frac{A_1 W - b}{A_2 a},
\]

and \(\tau = 1/(A_2 a)\) is the time scale for the response of \(S\). However, (3.53) can be applied only in saturated air (for condensation processes) because of the assumption of \(S \approx 1\).

We shall derive a general formula that can be applied to any \(S\) values. Let us rewrite the saturation development equation as

\[
\frac{dS}{dt} = S \left( \frac{l_v}{c_p T} - 1 \right) \frac{M_s g}{R T} W - (S \frac{l_v^2}{c_p R T^2} + \frac{P_{air}}{e_s})(aS + b), \tag{3.54}
\]

which is rearranged into

\[
\frac{dS}{dt} = \alpha S^2 + \beta S + \gamma, \tag{3.55}
\]

where

\[
\alpha = -\frac{l_v^2}{c_p R T^2} a,
\]

\[
\beta = \left( \frac{l_v}{c_p T} - 1 \right) \frac{M_s g}{R T} W + \frac{l_v^2}{c_p R T^2} b - \frac{P_{air}}{e_s} a,
\]

\[
\gamma = \frac{P_{air}}{e_s} b.
\]
To solve this first-order nonlinear differential equation, we can let

\[ \int dt = \int \frac{dS}{\alpha S^2 + \beta S + \gamma}. \quad (3.56) \]

For \( \beta^2 - 4 \alpha \gamma > 0 \), the term on the right-hand-side turns out to be

\[ \int \frac{dS}{\alpha S^2 + \beta S + \gamma} = \frac{1}{B_1} \ln \left| \frac{2\alpha S + \beta - B_1}{2\alpha S + \beta + B_1} \right|. \quad (3.57) \]

where

\[ B_1 = \sqrt{\beta^2 - 4\alpha \gamma}. \]

Integrating (3.56) from \( t = 0 \) to \( \Delta t \) and \( S = S_0 \) to \( S_1 \), we can derive

\[ \frac{2\alpha S_1 + \beta - B_1}{2\alpha S_1 + \beta + B_1} = \frac{2\alpha S_0 + \beta - B_1}{2\alpha S_0 + \beta + B_1} \exp(B_1 \Delta t) \equiv B_2. \quad (3.58) \]

The saturation ratio after time \( \Delta t \) is thus

\[ S_1 = \frac{1}{2\alpha} \left( \frac{2B_1}{1 \pm B_2} - \beta - B_1 \right). \quad (3.59) \]

The correct sign in the denominator can be determined by inserting \( S_1 \) back into (3.58) to make sure that \( B_2 > 0 \).

The quasi-analytical solutions discussed above can be quite useful in predicting the saturation ratio at a time step ahead. However, the prediction can be inaccurate when the growth rate is so large such that \( a \) and \( b \) can not be considered constant during one time step. The following section introduces a method that can predict the saturation ratio without knowing \( a \) and \( b \).
3.2.2. Environmentally Determined Growth Method

The number of governing equations needed to calculate the diffusional growth in the particle framework is multiplied by the total number of drop categories. Normal predictor-corrector and iterative methods require error-checking on all parameters in each system to determine the criterion for convergence. However, the diffusional growth of each particle is controlled by the gas-phase parameters and is not directly influenced by the growth of other particles. In other words, all particle systems are linked through the gas-phase parameters. As long as the gas-phase parameters are determined accurately, the calculation of the growth of each particle should also be correct.

The environmentally-determined growth method checks the error only on the gas-phase parameters. This method works not only on the condensational growth of particles from water vapor but also on the kinetics of trace-gas mass transfer. It has the further advantage of reducing numerical instability caused by some terms that produce large individual errors, which might be insignificant relative to the overall process. Combined with the forecasting method that will be discussed next, the environmentally determined growth method can drastically reduce the computational time.

Forecasting Method

The evolution of the gas-phase parameters (e.g., $S$, $T$, $P$, etc.) is usually a smooth function within a few time steps. It is possible to give good predictions on such parameters for a short time ahead. The forecasting method described below predicts the gas-phase parameters by using past records. An immediate application of such technique is to predict the average saturation ratio during one time step, and thus to derive the pseudo-growth rate that will be discussed in the next section.
Statistical forecasting methods are based on the history of past data. The data set is updated after every new calculation or observation. Extrapolation methods using polynomials or splines need only a few observed data points to gain high-order approximation, but are too sensitive to small perturbations. Using a large set of preceding data may produce a more stable trend but could impose a computational resource limitation. However, there are many existing forecasting techniques that use large data sets to produce smooth predictions, such as the moving average methods and the exponential smoothing methods (Makridakis and Wheelwright, 1978, pp. 44-71).

The disadvantage of the moving-average methods is the requirement to save a large set of data points and the application of equal weights to each data value. Exponential smoothing, however, can distill large data set into a few parameters, which give decreasing weights to data further from the present. For such reasons, the exponential smoothing techniques are preferred in this study to the moving-average method.

The method used here is called the **Brown’s quadratic exponential smoothing** method (BQES). This technique makes forecasts based on the quadratic formula (Brown, 1963, pp. 140-144):

\[
F_{t+\delta t} = a_t + b_t \delta t + c_t \delta^2 t,
\]

\[
a_t = 3Z'_t - 3Z''_t + Z'''_t
\]

\[
b_t = \frac{\alpha}{2(1-\alpha)^2} [ (6-5\alpha)Z'_t - (10-8\alpha)Z''_t + (4-3\alpha)Z'''_t ]
\]

\[
c_t = \frac{\alpha^2}{2(1-\alpha)^2} [ Z'_t - 2Z''_t + Z'''_t ]
\]

where \(F_{t+\delta t}\) is the forecast for time \(t+\delta t\), \(\alpha\) is a weighting function, which will be discussed later, and the single, double, and triple moving averages are defined as
\[ Z'_i = \alpha Z_i + (1 - \alpha)Z'_{i-1}, \]
\[ Z''_i = \alpha Z'_i + (1 - \alpha)Z''_{i-1}, \]
\[ Z'''_i = \alpha Z''_i + (1 - \alpha)Z'''_{i-1}, \]

where \( Z_i \) is the current calculated or observed value and subscript \( t-1 \) denotes the moving averages of the last time step. These moving averages represent all values in the past with weight decreasing exponentially with the length of time from the present (i.e., each data point is weighted \(1 - \alpha \) times less after each time step). The smoothing constant \( \alpha \) has a value between zero and one, depending on the nature of the forecasted variable. One can find the optimal value by a few trials. An \( \alpha \) of 0.4 ~ 0.7 is found to be suitable for the forecasting of the air properties such as temperature, pressure, and saturation ratio for the study of cloud microphysics. One can even design an \( \alpha \) that varies according to the linearity of the predicting parameters. The forecasted results in this study are generally accurate (at least to the fifth digit) for a typical time step of one second. To forecast the average value, \( \bar{F} \), during the time step \( \delta t \), we can either simply take the average of \( S_t \) and \( F_{t+\delta t} \), or apply the mean value theorem to (3.60) so that

\[ \bar{F} = \frac{\int_0^{\delta t} F(t) \, dt}{\int_0^{\delta t} \, dt} = a_t + \frac{b_t}{2} \delta t + \frac{c_t}{3} \delta t^2. \] (3.62)

The conventional implementation of (3.60) requires a constant time-step. With a minimal of adjustment, however, the BQES method can be adapted to use variable time-steps. Supposing that we want to use a new time step \( \delta t^* = n \delta t \), where \( n \) can be either greater or less than one, the forecast value would be:

\[ F_{t+\delta t^*} = a_t + b_t \delta t^* + c_t (\delta t^*)^2 = a_t + b_t n \delta t + c_t (n \delta t^2). \] (3.63)
To update the moving average, it can be proved that (3.60) remains the same with $Z_t$ being the actual calculated (or observed) value at time $t+n\delta t$. The only parameter needed to be modified is the current time step, which should be updated to $\delta t^*$. The advantages of the BQES method are (1) only the three moving averages and $\alpha$ (plus the previous time step if using variable time steps) need to be saved; (2) that it allows for variable time steps and a variable smoothing constant; and (3) it is generally stable and accurate. Occasionally, when strong variations exist in the trend, the method might be unstable. In the case of condensational growth, an over-prediction of saturation ratio may result in an over-depletion of water vapor and a low calculated saturation ratio. The forecasted value and the calculated value, therefore, tend to deviate from the actual value in the opposite direction. Such oscillation might become unstable in extreme conditions. By blending in about 30% of the forecasted value with the calculated value $Z_t$ for updating the first moving average $Z'_t$, we can dampen out such instability.

### 3.2.3. Quasi-Analytical Solution for the Diffusional Growth Equation

The mass growth and heat transfer equations for the diffusional growth of droplets are implicitly interdependent through the drop temperature and cannot be solved analytically. The purpose of this exercise is to first transform the diffusional mass growth equations into a set of explicit first-order nonlinear differential equations, then use the mean value theorem to derive a quasi-analytical solution.

Putting the modification factors aside, the diffusional mass growth equation is rewritten here as

$$
\frac{dm}{dt}\bigg|_{\text{diff}} = \frac{4\pi D_v f_v}{M_w} (\rho_v - \rho_w) = 4\pi r \frac{D_v f_v}{\mathcal{R}} \left( \frac{e_x - e_w}{T_x} \right) \left( \frac{T_x}{T_w} \right), \quad (3.64)
$$
where $\rho_w$ is the vapor density immediately over the drop surface, $e_w$ is the saturation vapor pressure over the drop surface, and $m$ is the drop mass (in mole). According to the Köhler's equation, discussed in Section 2.2.1, the saturation vapor pressure can be expressed as

$$e_w = e_{s,w}(T_w) f_{Köh},$$

(3.65)

where $e_{s,w}(T_w)$ is the water-saturation vapor pressure at temperature $T_w$, and

$$f_{Köh} \equiv \exp\left(\frac{\sigma_{wa}}{R_s T_w \rho_w r} \frac{n_w}{n_w + i s n_s}\right) \approx \exp\left(\frac{\sigma_{wa}}{R_s T_w \rho_w r} \left(1 - \frac{i s n_s}{n_w}\right)\right)$$

$$\approx \exp\left(\frac{\sigma_{wa}}{R_s T_w \rho_w r} \exp\left(-\frac{i s n_s}{n_w}\right)\right) \equiv \exp(y).$$

(3.66)

The parameter $y$ can be expressed in terms of the drop radius:

$$y = \frac{\alpha}{r} - \frac{\beta}{r^3},$$

(3.67)

where

$$\alpha = \frac{\sigma_{wa}}{R_s T_w \rho_w}, \text{ and } \beta = \frac{M_w \rho_s i s r^3}{M_s \rho_w}.$$

On applying the Clausius-Clapeyron equation, we rewrite the saturation vapor pressure as

$$e_{s,w}(T_w) = e_{s,w}(T_\infty) \exp\left[\frac{l_v}{R_s} \frac{(T_w - T_\infty)}{T_w T_\infty}\right] \equiv e_{s,w}(T_\infty) f_{CC}.$$

(3.68)

Letting the temperature difference between the drop and air be $\Delta T$, we have

$$T_w \equiv T_\infty + \Delta T \equiv T_\infty \left(1 + \delta\right),$$

(3.69)

where $\delta = \Delta T / T_\infty$. After applying a first-order Taylor's series approximation, $e_w$ can be rewritten as
\[ e_w = e_{s,w}(T_{\infty}) f_{Koh} f_{CC} = e_{s,w}(T_{\infty}) \exp \left[ y + \frac{l_v}{\mathcal{R}(1+\delta)} T_{\infty} \right] \]
\[ \approx e_{s,w}(T_{\infty}) \left[ 1 + y + \frac{l_v}{\mathcal{R}(1+\delta)} T_{\infty} \right] . \]  
(3.70)

Since \(|\delta| \ll 1\) typically, we have \(\frac{1}{1+\delta} \approx 1 - \delta\) and the mass growth equation can be rewritten as
\[ \frac{dm_w}{dt}_{\text{diff}} = 4 \pi r \frac{D_v e_{s,w}(T_{\infty})}{\mathcal{R} T_{\infty}} \left[ S_{\infty} - (1-\delta) \left( 1 + y + \frac{l_v}{\mathcal{R} T_{\infty}} \delta (1 - \delta) \right) \right] . \]  
(3.71)

Also note that \(y \ll 1\) under normal conditions. We may thus ignore the second-order terms of \(\delta\) and \(y\) to get
\[ \frac{dm_w}{dt}_{\text{diff}} = 4 \pi r \frac{D_v e_{s,w}(T_{\infty})}{\mathcal{R} T_{\infty}} \left[ S_{\infty} - (1-\delta) - \delta (1 - \delta) \right] . \]  
(3.72)

Now let us examine the heat transfer equation
\[ \frac{dH_w}{dt} = 4 \pi r k_a f_h \left( T_{\infty} - T_w \right) + h_v \frac{dm_w}{dt}_{\text{diff}} . \]  
(3.73)

By separation of variables, the total derivative of the total heat \((H_w = m_w h_w)\) can be expressed as
\[ \frac{dH_w}{dt} = h_w \frac{dm_w}{dt}_{\text{diff}} + m_w \frac{dh_w}{dt} . \]  
(3.74)

The second term on the right-hand-side can be found to be negligible so that
\[ 4 \pi r k_a f_h \left( T_{\infty} - T_w \right) + h_v \frac{dm_w}{dt}_{\text{diff}} \approx h_w \frac{dm_w}{dt}_{\text{diff}} . \]  
(3.75)

We can now derive \(\delta\) as
\[ \delta = \frac{T_w - T_{\infty}}{T_{\infty}} = \frac{l_v}{4 \pi r k_a f_h T_{\infty}} \frac{dm_w}{dt}_{\text{diff}} . \]  
(3.76)
(recall that \( l_v = h_v - h_w \)). Inserting the above equation back into (3.72), we get

\[
\frac{dm_w}{dt} \bigg|_{\text{diff}} \approx 4 \pi r \frac{S_\infty - (1+y)}{A},
\]

where

\[
A = \frac{\mathcal{R}T_\infty}{D_v f_e e_{ap} (T_e)} + \frac{l_v}{k_v f_h T_e} (\frac{l_v}{\mathcal{R}T_e} - 1). \quad (A \sim 10^7 \text{ s m kg}^{-1})
\]

Knowing that \( \frac{dm_w}{dt} = 4 \pi r^2 \frac{dr}{dt} \rho_w \), the mass growth equation can now be transformed into a first-order, nonlinear differential equation:

\[
\frac{dr}{dt} = \frac{B}{r} \left( S_\infty - 1 - \frac{\alpha}{r} + \frac{\beta}{r^3} \right), \quad (3.78)
\]

where \( B \equiv 1/(A \rho_w) \) (\( B \sim 10^{10} \text{ m}^2 \text{ s}^{-1} \)) is independent of \( r \). Numerical methods such as Euler’s method or the higher-order Runge-Kutta method, can be used to solve this ordinary differential equation. However, the time step required is still quite small, especially during the activation or evaporation of drops. An alternative method is, therefore, introduced here which utilizes the mean value theorem to derive a quasi-analytical solution.

1. **Mean-value Theorem Method**

   Assuming that the growth of drops can be determined by the average environmental parameters \( T, P, \) and \( S_\infty \) in one time step, which can be derived by using the forecasting method mentioned in last section. We can, therefore, treat \( B, S_\infty, \alpha, \) and \( \beta \) in (3.78) as constant. The change of radius \( \delta r \) during one time step \( \delta t \) can then be approximated by:

\[
\delta r = \overline{\left( \frac{dr}{dt} \right)} \delta t, \quad (3.79)
\]

where \( \overline{\left( \frac{dr}{dt} \right)} \) is the average rate change of \( r \) during a time step \( \delta t \) and is a function of \( r \) only. Applying the mean value theorem, we can express the growth equation in a
finite-difference form:

\[ \frac{\delta r}{\delta t} \approx \left( \frac{dr}{dt} \right) = \frac{\int_{r_0}^{r_1} \frac{dr}{dr} \, dr}{\int_{r_0}^{r_1} dr} = \frac{\int_{r_0}^{r_1} \frac{dr}{dt} \, dr}{\int_{r_0}^{r_1} \frac{dr}{dr}} = \frac{B}{\delta r} \int_{r_0}^{r_1} \left( \frac{S_\infty - 1}{r} - \frac{\alpha}{r^2} + \frac{\beta}{r^4} \right) dr \]

\[ = \frac{B}{\delta r} \left[ (S_\infty - 1) \ln r + \frac{\alpha}{r} + \frac{\beta}{3 r^3} \right]_{r_0}^{r_1}, \quad (3.80) \]

where \( r_0 \) and \( r_1 \) are the initial and final radii, respectively, and \( \delta r = r_1 - r_0 \). We thus have:

\[ (\delta r)^2 = (r_1 - r_0)^2 = \delta t B \left[ (S_\infty - 1) \ln \frac{r_1}{r_0} + \alpha \left( \frac{1}{r_1} - \frac{1}{r_0} \right) - \frac{\beta}{3} \left( \frac{1}{r_1^3} - \frac{1}{r_0^3} \right) \right], \quad (3.81) \]

which can be solved for \( r_1 \) using Newton’s method with \( r_0 \) as the initial guess. This method can increase the maximum time step to at least 10 times that required for a brute-force method for the calculation during the activation stage of cloud drops.

2. Square Root Analytical Solution

Although the quasi-analytical solution is even more accurate when used for activated large drops, there exists a much simpler analytical solution. For large and diluted drops, we can ignore the Kelvin and Raoult effects so that \( \Delta S \approx S_\infty - 1 \) is independent of \( r \). The growth equation then reduces to:

\[ \frac{d(r^2)}{dt} = 2 r \frac{dr}{dt} = 2 B \Delta S . \quad (3.82) \]

We thus derived the square-root solution:

\[ r_1 = \sqrt{r_0^2 + 2 B \Delta S \delta t} . \quad (3.83) \]

Hagen (1979) used the criterion \( r > r^\# \equiv r^* + 2 \mu \text{m} \) to decide if the drop can be regarded as large and dilute. The parameter \( r^\# \) is called the dividing radius.
3.2.4. Limited Growth of Haze Particles

There actually are no distinct physical or chemical differences between the haze particles and the cloud drops. As described in Section 2.2.1 and 2.2.2, the only thing that distinguishes haze particles from the activated drops is their position on the Köhler curve. Haze particles are stable as long as the saturation ratio in the air is between the deliquescence point and the critical saturation ratio. Under any perturbation of the saturation ratio, haze particles do not grow indefinitely but tend to reach their new equilibrium sizes. For small haze drops, the adjustment to a new equilibrium size can be considered to be instantaneous under normal cloud modeling time steps. This is not true, however, for large haze particles. As will be discussed in Section 3.5.1, the characteristic time for condensational growth is given as

\[ \tau_{\text{cond}} \sim \frac{C r^2}{\Delta S}, \tag{3.84} \]

which shows it has an \( r^2 \) dependence. However, the saturation ratio offset \( \Delta S \) also varies with the size of the haze particles. A detailed calculation of the time constant is done by applying the saturation development equation (3.48):

\[ \frac{dS}{dt} = A_1 W - A_2 \frac{dy_{w}}{dt}. \tag{3.85} \]

Combining this equation with the growth equation (3.78), we can estimate the time constant by suddenly applying a constant updraft of \( W = 2 \text{ m s}^{-1} \) to the air parcel. As shown in Table 3.3, the time constant \( \tau \) generally increases with the amount of solute (as indicated by the dry size \( R \)) in the haze particle. It also decreases with time as the saturation ratio offset \( \Delta S \) gradually builds up. For a time period of less than one second, the time constant is quite large but the actual size does not deviate too far from the equilibrium size. As the supersaturation builds up, the time constant decreases as a
result of an increase in the driving force $\Delta S$. Haze drops with small solute content have very small time constants after a time period of more than 1 second and do not deviate much from their equilibrium sizes. Haze particles with a dry size larger than one $\mu$m have time constants that are significantly longer than the time steps normally used in cloud modeling and, therefore, always lag in reaching their equilibrium sizes. Note that the time constant varies with the relative humidity and is a combined effect of the change of both $r$ and $\Delta S$ in (3.84). So, we should not assume that large haze drops stay at their equilibrium sizes in the updraft. The kinetic growth equation (3.78) should be applied even for the growth of haze particles. However, numerical errors tend to occur in calculating the growth of small haze drops because of their very small time constant. Fortunately, we know that the growth of haze particles is stable and will at most reach the equilibrium sizes. So, the equilibrium size can be used as a constraint for the growth of haze particles.

Table 3.1: Time constants for the condensational growth of ammonium-sulfate haze particles, expressed in terms of the dry sizes, $R$, initial relative humidities, and the time $\Delta t$ after the start of air ascending at a rate of $W = 2.0$ m s$^{-1}$ with standard conditions of $T = 273.15$ K, and $P = 1000$ mb.
3.2.5. Bin Split for Drop Activation

With the bin method introduced in Section 3.1, the mean growth of the drops in a bin is represented by the growth of the mean. This normally implies that all drops in the same bin will grow or decay at the same rate. However, whether a drop can be activated or not at a certain saturation depends on their solute content. It is possible that only a portion of the drops in one bin can be activated. Let us consider the solute component of a particular bin, which has $R_1$ and $R_2$ as the lower and upper bin limits (in terms of the dry particle size $R$). The Köhler curves for droplets with dry-sizes of $R_1$ and $R_2$ are shown in Figure 3.17. When the environmental saturation ratio $S_{\infty}$ lies in between the maximum (critical) saturation ratios $S^*$ of the two curves, only particles that have an $S^*$ less than $S_{\infty}$ can be activated. Let $R_{\text{act}}$ be the dry-size of a haze particle that has a critical saturation ratio that equals $S_{\infty}$, then the criterion for a drop to be activated is $R > R_{\text{act}}$ or $S^* < S_{\infty}$. If we set $\frac{dr}{dt}$ in equation (3.78) equal to zero, we can derive a simplified Köhler theory equation:

$$S = 1 + \frac{\alpha}{r} - \frac{\beta}{r^3}, \quad (3.86)$$

where $S$ is the equilibrium saturation ratio and $r$ is the drop radius. By taking the first derivative of (3.) with respect to $r$ equal to zero, we can write the critical radius that correspond to the critical saturation ratio as:

$$r^* = \sqrt[3]{\frac{3\beta}{\alpha}}. \quad (3.87)$$

The critical saturation ratio $S^*$ is then obtained by inserting $r^*$ back into (3.86) such that

$$S^* = 1 + \frac{\alpha}{r^*} - \frac{\beta}{(r^*)^3} = 1 + \frac{2\alpha}{3r^*} = 1 + \frac{2}{3} \sqrt[3]{\frac{\alpha^3}{3\beta}}. \quad (3.88)$$
As given in (3.67), $\beta$ is a function of the dry particle radius ($\beta = \frac{M_w \rho_s r^3}{M_p \rho_w}$). We can thus find $R_{\text{act}}$ by letting $S^* = S_\infty$ to get

$$R_{\text{act}} = \alpha \left[ \frac{4M_p \rho_w}{27M_w \rho_s \left(S_\infty - 1\right)^{1/2}} \right]^{1/3}$$

(3.89)

which is a function of air temperature and saturation ratio. For any solute bin that has its limits enclosing $R_{\text{act}}$ ($R_1 < R_{\text{act}} < R_2$), we must split the bin so that only particles with $R > R_{\text{act}}$ are allowed to be activated. The total number of particles being activated can then be calculated by integrating the distribution function from $R_{\text{act}}$ to $R_2$.

---

**Figure 3.17:** Schematic diagram of the situation when a bin-split should be performed. The two thick curves are the Köhler curves for particles with dry-size at the two bin-limits $R_1$ and $R_2$. The gray curve indicates the minimum dry-size for a haze drop to be activated at a saturation ratio of $S_\infty$ (the dotted-line).
3.3. Numerical Methods for the Hydrodynamic Interactions

The stochastic approach, as mentioned in Section 2.2.3, is commonly used to represent the hydrodynamic interactions between cloud particles. However, the interpretation of the numerical results from such approach is not straightforward. We will discuss the details of the collection problems in this section.

3.3.1. Drop Coalescence

1. Fortunate Drops

Early theoretical work on the collision-coalescence problem seemed to indicate that the growth of drops from the coalescence process proceeds too slowly to account for the appearance of raindrops. Nevertheless, Telford (1955) pointed out that the probabilistic appearance of a relatively few fortunate drops is sufficient to produce large rain drops in a reasonably short amount of time. The number concentration of raindrops is normally on the order of $10^3$ m$^{-3}$ while that for cloud drops is on the order of $10^9$ m$^{-3}$. Therefore, the formation of raindrops starts from those one-in-a-million most “fortunate” cloud drops. These fortunate drops are initially only a subset of the cloud drop population but are statistically determined to grow faster than the others. During the lifetime of a typical precipitation drop, at least a million collision-coalescence events may be needed to form 1 mm drops from a population of 10 µm cloud drops. Such a large amount of collection is possible only when the drops reach large enough sizes to gain an appreciable fall velocity and a reasonable collection efficiency. Therefore, the existence of the fortunate drops that take an early start in growing may be very important to the initiation of rain formation, especially from warm clouds.
Given \( N_1 \) and \( N_2 \) as the number concentrations in drop groups of size \( r_1 \) and \( r_2 \), the total number of collisions \( N_{\text{coll}} \) occurring in a given time interval can be obtained using the quasi-stochastic approach discussed in Section 2.3.2. For \( r_1 < r_2 \) and \( N_1 > N_2 \), there are three inequalities existing among \( N_1 \), \( N_2 \), and \( N_{\text{coll}} \), which require special attention. In the first situation, where \( N_{\text{coll}} > N_1 \), the collision frequency is so high that all drops in each group have a multiple chance to collide with other drops. Such conditions are very uncommon in real clouds, and could be a result of using unreasonably large time-steps. In the second case, \( N_1 > N_{\text{coll}} > N_2 \), the number of collision is greater than the total number of large drops. This happens when large drops have reached significant sizes to collect more than one drop at a single time step, but only a fraction of the small drops is collected. One must be careful not to interpret \( N_{\text{coll}} \) as the number of large drops that underwent collision. In the third case, \( N_{\text{coll}} < N_2 \), only a few drops from each group have the chance to collide with each other. It would be erroneous to divide the mass of the collected drops among all large drops. Classical methods that ignored this fact usually resulted in an impeded rain formation.

Let us examine the collection rates in order to quantify the definition of the fortunate drops. The rate for each large drop to collide with smaller drops is the product of the collision kernel \( K_{\text{coll}} \) and the number concentration \( N_1 \) of the drops to be collected:

\[
\dot{N}_2 = \pi (r_1 + r_2)^2 E_c \Delta V_\infty N_1 = K_{\text{coll}} N_1 ,
\]

(3.90)

where \( E_c \) is the collision efficiency and \( \Delta V_\infty \) is the relative fall velocity. Figure 3.18 shows the change of \( \dot{N}_2 \) as a function of \( r_2 \), with a typical \( N_1 \) of \( 10^9 \) m\(^{-3} \) and values for \( E_c \) from Shafrir and Neiburger (1963). The collision rate \( \dot{N}_2 \) increases monotonically with the size of the collector drops. The change of \( \dot{N}_2 \) is larger at smaller drop sizes and decreases toward larger sizes. Drops larger than about 40 µm can collect more than one cloud drop using a typical time step of 1 second.
Figure 3.18: Collision rate for drops of different sizes collecting cloud drops. The three curves are for $r_1 = 10 \, \mu m$, 20 \, \mu m, and 30 \, \mu m$, respectively.
Another parameter that can help determine the importance of the fortunate drops is the time required for drops to grow to a precipitable size. Figure 3.19 shows the time evolution of the drop-size due to collision-coalescence in an environment with 1 g m$^{-3}$ liquid water content and monodispersed cloud drops of 10 µm in radius. The time required for a drop of 20 µm in radius to grow to 40 µm is about 30 minutes, from 40 µm to 100 µm is about 13 minutes, and from 100 µm to 1 mm is about 23 minutes. Evidently, the growth rate increase dramatically after the drop reaches about 40 µm, a size that gives a one per second collection rate.

Figure 3.19: Time evolution of drop size due to growth by collision-coalescence.
2. **Numerical Determination of the Fortunate Drops**

The probability of collision is described by a binomial distribution that is similar to the outcome of a coin-tossing experiment:

\[
P(n) = \frac{x!}{n! \left( x - n \right)!} p^n q^{x-n}, \quad (3.91)
\]

where \( x (= N_{\text{coll}}) \) is the total number of trials (collisions) in a given time interval, \( n \) is the number of small drop collected by one large drop, \( p \) is the probability for each small drop to hit any particular large drop \( (= \frac{1}{N_2}) \), and \( q = 1 - p \). This binomial distribution can be approximated by a normal distribution function

\[
P(n) = \exp \left\{ - \left( \frac{n-\mu}{\sigma} \right)^2 \right\}, \quad (3.92)
\]

where \( \mu = xp \) is the mean number of drop collected by the large drop and \( \sigma = \sqrt{xpq} \) is the standard deviation. Note that this approximation can be used if \( x \geq \frac{5}{\min(p,q)} \).

However, it is difficult to apply such distribution functions to the stochastic growth equation. A simplified scheme is thus needed.

The chance of a small drop to hit any particular collector drop is normally very small so that \( p \ll 1 \) and \( q \approx 1 \). The standard deviation \( \sigma \), which is a measure of the spread of the distribution, can now simplified as

\[
\sigma \approx \sqrt{xp} = \sqrt{\frac{N_{\text{coll}}}{N_2}} \quad (3.93)
\]

by letting \( q = 1 \). One can find that, when \( N_{\text{coll}} \) is much smaller than \( N_2 \), the probability is a narrow distribution that is centered near \( n = 0 \) and there is a small chance for \( n = 1 \). This means that most drops do not engage in collection at all. Only a few drops have the chance to collect one other drop. The chance of collecting two or more drops \( (n \geq 2) \) is negligible. We can treat the collection process as purely a one-to-one interaction.
When $N_{\text{coll}}$ is larger than $N_2$, the spreading of the probability distribution could be large. However, this large spreading might not be important at all. A drop collecting 100 small drops does not gain a mass that is too much different from a drop collecting 105 drops despite there being a difference of 5 drops. Besides, such a situation occurs when the collector drops are already very large and hence not important to the initiation of precipitation. We should look at the normalized standard deviation instead:

$$
\frac{\sigma}{\mu} = \sqrt{\frac{q}{pX}} \approx \sqrt{\frac{1}{pX}} = \sqrt{\frac{N_2}{N_{\text{coll}}}}.
$$

(3.94)

Now, the relative spreading is small for $N_{\text{coll}} \gg N_2$. In this case, we can assume that all large drops collect the same number of small drops, which is simply $N_{\text{coll}} / N_2$. As before, the collected total mass can be assumed to be distributed evenly among all the collector drops.

The situation that drops under the same conditions collect different amounts of mass occurs when $N_{\text{coll}}$ is of about the same order of magnitude as $N_2$. This means that there are fortunate drops among the fortunate drops -- the most fortunate drops. The collection rate that corresponds to an $N_{\text{coll}} = N_2$ is exactly one per time step, a rate that indicates the initiation of precipitation formation. So, the distinction for these most fortunate drops becomes important at the most critical stage for precipitation formation. In the next section, we will discuss how to deal with the most fortunate drops, along with some other similar problems.
3.3.2. **Adjustment for the Overlapped Collection**

In the previous section, we considered only two groups of drops in demonstrating the importance of the *fortunate* drops. However, in the categorical models, one drop group actually interacts with many other groups at the same time, resulting in a range of values for the ratio $N_{\text{coll}} / N_2$. Such multiple interactions impose two problems: 1) fractional and overlapped collections, and 2) competition. We will discuss the first problem here and the second problem in the next section.

The problem with the fractional and overlapped collections, just like the spreading of the collection probability function, is most serious when $N_{\text{coll}} / N_2$ is near unity. For small collision probabilities ($N_{\text{coll}} / N_2 \ll 1$), the overlapping is minimal. For multiple collections ($N_{\text{coll}} / N_2 \gg 1$), the overlapping is essentially the same for each large drop. Yet, when the probabilities are only partially overlapped, the number of combination of these probabilities is exponentially proportional to the number of the interacting drop groups, and is impossible to deal with. Let us assume that the collision ratio $N_{\text{coll}} / N_2$ for drop category 2 collecting category 1a, 1b, and 1c are 0.3, 0.6, and 0.9, respectively. Both the 30% $N_2$ that collect drop $N_{1a}$ and the 70% that do not will have 60% chance to collect drop $N_{1b}$ and 40% not to. In these four combinations, each will have a 90% chance to collect drop $N_{1c}$, and 10% that does not, etc. To avoid such complexity, we can make some simplifications based on previous analysis. First, we can separate the collected drops into groups that have (1) high collection rates, where $N_{\text{coll}} / N_2 > 10$, (2) moderate collection rate, where $10 \geq N_{\text{coll}} / N_2 \geq 1$, and (3) low collection rate, where $N_{\text{coll}} / N_2 < 1$, for collections that occurred during one typical time step. Then, each collector drop in group (1) is assumed to collect an even amount of mass. Besides these mean or ‘basic’ collections, some of the drops can also be in group (2) or (3) to collect additional mass. The number of collector drops involved in the group (3) collection is
simply \( \frac{N_{\text{coll}}}{N_2} \). For the moderate collection rates, two types of collections are assumed to reflect the spreading of the probability distribution function: (a) the integer part is treated like the high collection rate groups, and (b) the decimal part is treated as the low collection rate groups. To make a separation in such a manner is as if to assume the probability function to be distributed mostly over the first two discrete values, which normally covers more than 95% of the total probability. For example, an \( \frac{N_{\text{coll}}}{N_2} \) ratio of 6.8 will result in about 80% of the collector drops to collect 7 drops and nearly 20% to collect 6 drops. In practice, we separate such drops into two groups: (a) \( \frac{N_{\text{coll}}}{N_2} = 6.0 \), which is considered as the 'basic' collection; and (b) \( \frac{N_{\text{coll}}}{N_2} = 0.2 \), which is considered as the 'fractional' collection.

The next problem is that those 'fractional' collection events may overlap with each other. This not only occurs when the sum of all the fractions exceeds unity but also when it is smaller than one. Nevertheless, it is reasonable to assume that the chance of overlapping is small when the sum of the total fraction is very small. Having in mind that the whole purpose of this exercise is to identify the fortunate drops, we have a method that can reduce the complexity of the overlapping. The importance of the fortunate drops is that they can grow faster in mass than the others. We first sort the fractional collection drop groups according to the drop mass. Then, we select the largest-drop groups so that the sum of the total fraction is somewhat less than unity. These selected groups are considered as non-overlapping fractions. We can now think of drops in these groups as the most fortunate drops. The rest of the fraction can be considered inconsequential and are treated as the ‘basic’ collections.
3.3.3. **Adjustment for Over-Depletion**

Droplets in a certain bin may be over-depleted if one ignored the competition among all the collector drops. Let $P(i,j)$ represents the percentage of the number of drops in bin $j$ that can be collected by drops in bin $i$ without competition. Note that $P(i,j)$ is the parameter that one would normally use for the stochastic collection equation. The fraction left for the collection by drops in bin $k \neq j$ is then $1 - P(i,j)$. Because of the competition, however, the total amount of drops in bin $i$ being collected is not $\sum_j P(i,j)$, but should be expressed in the form of

$$P_i(i) = 1 - \prod_j (1 - P(i,j)).$$  

(3.95)

Therefore, the actual percentage of the number of drops in bin $j$ that can be collected by drops in bin $i$ should be

$$P(i,j) = P(i,j) \prod_{k \neq j} (1 - P(i,k)) \equiv P(i,j) \alpha. \tag{3.96}$$

From the above equation, one can see that the over-depletion $P(i,j) - P'(i,j)$ is most serious when $P(i,j)$ is large. This occurs when there is a large amount of large collector drops or when the time step used is too large. As long as $\sum_j P(i,j)$ is much less than one, the modification factor $\alpha$ can be simplified as

$$\alpha \approx 1 - \sum_{k \neq j} P(i,j). \tag{3.97}$$

If the over-depletion adjustment is not applied, one should use the criterion $\sum_j P(i,j) \ll 1$ to determine the time step for the hydrodynamic collections.
3.3.4. Limited Number of Collisonal Breakup

Aside from the situation of rebound, a drop may either coalesce or break up on colliding with other drops. When there is multiple collection, a drop can numerically experience both the coalescence and breakup processes during one time step. We will discuss how to determine if the drops should undergo coalescence or breakup. In their experimental studies, Low and List (1982a) showed that drops of diameter less than 0.1 mm hardly ever break up after collision. Since the number concentration of drops larger than 0.1 mm is at least 4 to 5 orders of magnitude smaller than that of cloud drops, the rate for any large drop to collide with a drop larger than 1 mm is very small. So, fortunately, the probability of a drop to have more than one chance to break up during one typical time step is very small. We can, therefore, apply the same criteria as selecting fortunate drops so that breakup occurs only during the "fractional collection" events.
3.4. **Numerical Methods for the Growth of Ice Crystals**

The growth of ice particles in clouds is much more complicated than the growth of liquid drops. First, ice particles can grow by acquiring water from all three phases: growth by vapor diffusion, collection of drops and other ice particles. Compared with the growth of droplets, the heat equation for the growth of ice particles requires an extra term to account for the latent heat released during riming. Second, ice particles can have many different shapes, a characteristic that complicates the hydrodynamic behavior and the diffusional growth of ice particles. This section shows some numerical methods that are helpful in solving the growth equations for ice particles.

3.4.1. **Quasi-Analytical Solutions for the Growth Equations**

The quasi-analytical solution for the growth of ice particles is derived in a somewhat different way from that for liquid drops because of the following two factors: (1) the latent heat release from the freezing of the collected supercooled-drops presents an extra term in the mass and heat transfer equations for the growth of ice particles, (2) the curvature and solute effects are insignificant for the depositional growth of ice. The mass growth and heat transfer equations can be written as:

\[
\frac{dm_i}{dt} = \frac{dm_i}{dt}\bigg|_{\text{acc}} + \frac{dm_i}{dt}\bigg|_{\text{diff}}
\]

\[
\frac{dH_i}{dt} = \frac{dH_i}{dt}\bigg|_{\text{acc}} + \frac{dH_i}{dt}\bigg|_{\text{diff}} + \frac{dH_i}{dt}\bigg|_{\text{cond}}
\]

where the subscripts denote accretion (acc), vapor diffusion (diff), and conduction (cond). For simplicity, let the accretion rates be constant during each time step, so then
\[ \frac{dm_i}{dt}_{\text{acc}} \equiv \dot{m}_{\text{acc}} = \text{constant}, \text{ and} \]
\[ \frac{dH_i}{dt}_{\text{acc}} = h_w \dot{m}_{\text{acc}} \equiv \dot{H}_{\text{acc}} = \text{constant}. \]

Other mass-growth and heating rates are expressed as:

\[ \frac{dm_i}{dt}_{\text{diff}} = \frac{4\pi CD_v f_v}{M_w} (\rho_{\infty} - \rho_i) = 4\pi C \frac{D_v f_v}{\mathcal{R}} \left[ \frac{e_{\infty}}{T_{\infty}} - \frac{e_{s,i}(T_i)}{T_i} \right], \quad (3.100) \]

\[ \frac{dH_i}{dt}_{\text{cond}} = 4\pi C k_{\ell} f_{\ell} (T_{\infty} - T_i), \text{ and} \quad (3.101) \]

\[ \frac{dH_i}{dt}_{\text{diff}} = h_v \frac{dm_i}{dt}_{\text{diff}}. \quad (3.102) \]

Similar to the procedure used in deriving the analytical solution for drop growth, the total heat change can be approximated as

\[ \frac{dH_i}{dt} = h_i \frac{dm_i}{dt} + m_j \frac{d\ell}{dt} \approx h_i \frac{dm_i}{dt} = h_i \left( \frac{dm_i}{dt}_{\text{diff}} + \frac{dm_i}{dt}_{\text{acc}} \right). \quad (3.103) \]

We can rearrange the heat transfer equation to get

\[ 0 = 4\pi C k_{\alpha} f_{\alpha} (T_{\infty} - T_w) + l_s \frac{dm_i}{dt}_{\text{diff}} + l_t \frac{dm_i}{dt}_{\text{acc}} \]

\[ = 4\pi C \left[ k_{\alpha} f_{\alpha} (T_{\infty} - T_i) + l_s D_v f_v \left[ \frac{e_{\infty}}{T_{\infty}} - \frac{e_{s,i}(T_i)}{T_i} \right] \right] + l_t \dot{m}_{\text{acc}}. \quad (3.104) \]

As before, \( l_s = h_v - h_i \) is the molar latent heat of sublimation and \( l_t = h_w - h_i \) is the molar latent heat of freezing. Let us define the temperature difference between the ice particle and air as \( \Delta T \) so that \( T_i = T_{\infty} + \Delta T = T_{\infty} (1+\delta) \), where \( \delta \equiv \frac{\Delta T}{T_{\infty}} \) is normally much less than
The saturation vapor pressure over ice, $e_{s,i}(T_i)$, can be obtained by applying the Clausius-Clapeyron equation

$$e_{s,i}(T) = e_{s,i}(T_\infty) \exp\left(\frac{l_s T_i - T_\infty}{R T_i T_\infty} \right) = e_{s,i}(T_\infty) \exp\left(\frac{l_s \delta}{R T_\infty} \right) . $$ \hspace{1cm} (3.105)

The exponential can be approximated by the first two terms of its Taylor's series expansion ($e^x \approx 1 + x$) such that

$$-k_s f_h T_x \delta + \alpha \left( S_{s,i} - \frac{1}{1 + \delta} \left[ 1 + \frac{l_s}{R T_\infty} \frac{\delta}{1 + \delta} \right] \right) + \frac{l_s m_{acc}}{4 \pi C} = 0 , \hspace{1cm} (3.106)$$

where $\alpha = l_s D_v e_{s,i}(T_\infty) / (R T_\infty)$ and $S_{s,i} = e_{s,i} / e_{s,i}(T_\infty)$, which is the ice-saturation ratio in the air. Since $\frac{1}{1+\delta} \approx 1 - \delta$ for $\delta \ll 1$, we get

$$-k_s f_h T_x \delta + \alpha \left( S_{s,i} - \left( 1 - \delta \right) \left[ 1 + \frac{l_s \delta (1 - \delta)}{R T_\infty} \right] \right) + \frac{l_s m_{acc}}{4 \pi C} = 0 . \hspace{1cm} (3.107)$$

The above equation is a cubic function of $\delta$, and has analytical solutions. However, it is permissible to ignore the third-order term to get the simpler solution:

$$\delta \approx -a_1 - \sqrt{a_1^2 - a_2} , \hspace{1cm} (3.108)$$

where

$$a_1 = \frac{1}{4} \left[ \frac{R T_\infty}{l_s} \left( 1 - \frac{k_s f_h T_x}{\alpha} \right) - 1 \right] , \hspace{1cm} \text{and}$$

$$a_2 = \frac{R T_\infty}{2 l_s} \left[ (S_{s,i} - 1) + \frac{l_s m_{acc}}{4 \pi C \alpha} \right] .$$

We thus derived an analytical solution, $T_i = T_\infty (1 + \delta)$, for the temperature of ice particle growing by both vapor diffusion and accretion. Under slow growing conditions, we can even ignore the second order terms so that $\delta \approx -a_2 / (2 a_1)$. Since the solute and
curvature effects are negligible for ice-phase particles, we can directly apply \( \delta \) to the diffusional growth equation:

\[
\frac{d m_i}{d t} \bigg|_{\text{diff}} \approx \frac{4\pi C D_y f_y e_{s,i}(T_x)}{R_x T_x} \left\{ S_{\pi,i} - (1 - \delta) \left[ 1 + \frac{L_i \delta(1 - \delta)}{R T_x} \right] \right\},
\]

\[ \text{(3.109)} \]

**Linearized Capacitance**

The above equation is still nonlinear because of the size and shape dependence of the capacitance \( C \). Nevertheless, it can be shown that the ratio of the capacitance \( C \) to the spherical-equivalent radius \( r_i \) of the ice particle (\( q \equiv C / r_i \)) is a slowly varying parameter and can be regarded as constant during a typical time-step. The analytical equation of the mass growth rate can thus be linearized by letting \( C = q r_i \). Recall that the capacitance of the ice particles can be expressed as:

- **prolate spheroid**: \( C = \frac{c \varepsilon}{\ln[(1+\varepsilon)c/a]} \), \( \varepsilon = (1 - \frac{a^2}{c^2})^{1/2} \);

\[ \text{(3.110)} \]

- **oblate spheroid**: \( C = \frac{a \varepsilon}{\sin^{-1}\varepsilon} \), \( \varepsilon = (1 - \frac{c^2}{a^2})^{1/2} \).

For a spherical particle, the aspect ratio \( \phi = 1 \) and eccentricity \( \varepsilon = 0 \), the capacitance is the same as the radius of the particle \( r_i \). Therefore, we will examine the variation of \( C \) only for the two extreme values of the aspect ratio. At the two extremes, where the eccentricity \( \varepsilon \rightarrow 1 \), we have
pporte spheroid: \( C = \frac{c}{\ln(2c/a)} \),

oblate spheroid: \( C = \frac{2a}{\pi} \).

Invoke the expression for the volume of a spheroid:

\[
V = \frac{4}{3} \pi r_i^3 = \frac{4}{3} \pi a^2 c = \frac{4}{3} \pi a^3 \phi \quad (= \frac{4}{3} \pi c^3 / \phi^2),
\]

and the relationship between the change of aspect ratio and volume (see Section 2.3.2.1):

\[
d\ln \phi = \frac{\Gamma-1}{\Gamma+2} d\ln V,
\]

where \( \Gamma \) is the inherent growth habit. Thus, we can derive the expression for \( q \) at the extreme values of \( \phi \):

prolate spheroid:

\[
q = \frac{C}{r_i} = \frac{\phi^{2/3}}{\ln(2\phi)} \approx \frac{4}{3} \phi^{2/3} (\phi \to \infty)
\]

oblate spheroid:

\[
q = \frac{C}{r_i} = \frac{2}{\pi \phi^{1/3}}.
\]

The change of \( q \) expressed in terms of the volume change is thus:

prolate spheroid:

\[
d\ln q = \frac{2}{3} d\ln \phi = \frac{2}{3} \frac{\Gamma-1}{\Gamma+2} d\ln V,
\]

oblate spheroid:

\[
d\ln q = -\frac{1}{3} d\ln \phi = -\frac{1}{3} \frac{\Gamma-1}{\Gamma+2} d\ln V.
\]

We can think of \( d\ln q (=dq/q) \) and \( d\ln V (=dV/V) \) as the fractional change of \( q \) and \( V \). Since \( \frac{\Gamma-1}{\Gamma+2} \) is always less than unity, the magnitude of the change of \( q \) is always less than that of the volume changes. Thus, we can assume that \( q \) is constant during a time step whenever the relative change of \( V \) is small. The relative change of volume can be large only when the ice particles are quite small. But in this situation, the aspect ratio would be quite close to unity and the change of \( q \) would then still be quite small.
Square-root solution

From above analyses, the diffusional growth equation can be simplified as a first-order differential equation

\[
\frac{dm}{dt}\bigg|_{\text{diff}} = 4\pi r^2 \rho_i \frac{dr}{dt} \approx \frac{4\pi r q D_x f_x e_x(T_x)}{\mathcal{R} T_x} \left\{ S_{\infty,i} - (1 - \delta) \left[ 1 + \frac{l_x \delta (1 - \delta)}{\mathcal{R} T_x} \right] \right\},
\]

(3.116)

where \( \rho_i \) is the ice density during deposition. This equation can be rearranged to give

\[
\frac{d(r_i^2)}{dt} \approx \frac{2 q D_x f_x e_x(T_x)}{\rho_i \mathcal{R} T_x} \left\{ S_{\infty,i} - (1 - \delta) \left[ 1 + \frac{l_x \delta (1 - \delta)}{\mathcal{R} T_x} \right] \right\} \equiv A,
\]

(3.117)

where A is independent of \( r_i \). We thus derived the square-root analytical solution for the equivalent radius of ice particles:

\[
r_i = \left[ r_{i,o}^2 + A \delta t \right]^{1/2}.
\]

(3.118)

Here, \( r_{i,o} \) is the initial equivalent radius and \( r_i \) is the radius after a time \( \delta t \).
3.4.2. **Bin-shift for the Aspect Ratio**

To apply the bin-shift scheme to the aspect ratios, it is necessary to know the functional form of the change of the aspect ratio: \(d\phi = f(\phi)\). We shall examine the problem for depositional growth and riming cases.

Recall the equation given in Section 2.3.2.1: \(d\ln\phi = \frac{\Gamma - 1}{\Gamma + 2} d\ln V\). We can see that the change of aspect ratio due to vapor deposition is constant with respect to \(\ln \phi\) since \(\Gamma\) and \(d\ln V\) are independent of \(\phi\). The bin shift is thus linear in the log-scale, and we have

\[
d\ln\phi_1 = d\ln\phi_2 = d\ln\bar{\phi},
\]

where \(\phi_1\) and \(\phi_2\) are the aspect ratios at the lower and upper bin limits, and \(\bar{\phi}\) is the mean aspect ratio, which is determined by the discrete growth method.

The scheme for the change of aspect ratio due to riming was discussed in Section 2.3.3. It was assumed that the length of the major axes is fixed during riming. Thus, \(c\) is constant for columnar ice and \(a\) is constant for planar ice. From the expression for the volume of spheroids

\[
V = \frac{4}{3} \pi a^2 c = \frac{4}{3} \pi a^3 \phi = \frac{4}{3} \pi c^3 / \phi^2,
\]

we can derive:

\[
d\ln V = -2 d\ln \phi \quad \text{for columns},
\]

\[
d\ln V = d\ln \phi \quad \text{for plates}.
\]

Therefore, the change of aspect ratio is also linear on a log scale for the growth of ice particles by riming. A similar conclusion can be reached in the case of melting. From the analyses given above, we see that the bin-shift method for the aspect ratio can be best performed in a log-scale.
3.5. Numerical Methods for the Aqueous-Phase Chemistry

In this section, we will first examine the characteristic times of various microphysical and chemical processes. A numerical method is then introduced to solve a set of equations that have very different characteristic times. Finally, a method is introduced to combine the equations for the equilibrium chemistry and kinetic reactions.

3.5.1. Characteristic Times

In numerical simulations, it is necessary to identify the characteristic time of the processes considered. Such identification helps us to determine the appropriate numerical methods and time steps of integration, as well as the possible simplifications for certain trouble-causing mechanisms. For a microphysical model, the characteristic times for various microphysical processes are obviously the ideal reference for other processes. Chemical processes that have a time scale much smaller than the smallest time scale among the microphysical processes can be assumed to achieve equilibrium instantaneously.

Considering the simplified form of the condensation growth equation:

\[
\frac{dr}{dt} = C \frac{\Delta S}{r},
\]

we can express the characteristic frequency as

\[
\kappa_{\text{cond}} \sim \frac{1}{r} \frac{dr}{dt} = C \frac{\Delta S}{r^2},
\]

where \( C \) is a constant, \( \Delta S \) is the supersaturation, and the characteristic time is

\[
\tau_{\text{cond}} = \frac{1}{\kappa_{\text{cond}}},
\]
The time constant $\tau\text{\textsubscript{cond}}$ for condensation at $\Delta S = 1\%$ is about 1.7 s for $r = 1$ $\mu$m, and 170 s for $r = 10$ $\mu$m. In the event of evaporation, however, the smallest $\tau\text{\textsubscript{cond}}$ is about ten times less in an environment of 90% relative humidity.

With hydrodynamic collection, the growth rate for large drop A collecting small drop B can be expressed as

$$\frac{dm_A}{dt} = Ec \pi (r_A+r_B)^2 |(V_A-V_B)| \text{LWC},$$  \hspace{1cm} (3.125)

where $m_A$ is the mass of the drop A, $Ec$ is the collection coefficient, $r$ is the radius, $V$ is the terminal velocity, and LWC is the liquid water content in the air. The characteristic frequency for hydrodynamic collection is thus

$$\nu\text{\textsubscript{coll}} \sim \frac{1}{m_A} \frac{dm_A}{dt} \sim Ec \pi r_A^2 V_A \text{LWC} / m_A. $$ \hspace{1cm} (3.126)

The characteristic time $\tau\text{\textsubscript{coll}} = 1/\nu\text{\textsubscript{coll}}$ is about 1000 s for 10 $\mu$m drops, 170 s for 100 $\mu$m drop and 180 s for 1 mm drop for an $Ec \sim 1$ and LWC $\sim 1$ g kg$^{-1}$.

There are several aspects of the mass transfer problem in cloud chemistry. First, there is the diffusion of gaseous species to the surface of the droplet, for which the characteristic time is given as (Seinfeld, 1986, p. 253)

$$\tau_d = \frac{r^2}{4Dg}. $$  \hspace{1cm} (3.127)

For a typical gas diffusion coefficient $D_g$ of 1$\times$10$^{-5}$ m$^2$ s$^{-1}$, $\tau_d$ is 2.5$\times$10$^{-6}$ s, 2.5$\times$10$^{-4}$ s, and 2.5$\times$10$^{-2}$ s for drops of $r = 10$ $\mu$m, 100 $\mu$m, and 1 mm, respectively. When the gas molecules are adsorbed onto the drop surfaces, they tend to establish phase equilibrium at the gas-liquid interface, with a characteristic time $\tau_p$ given as (Seinfeld, 1986, p. 259)

$$\tau_p = D_g \left(\frac{4\pi TH}{\alpha c}\right)^2 \tau_p, $$  \hspace{1cm} (3.128)
where $D_l$ is the aqueous-phase diffusion coefficient (typically $= 10^{-9}$ m$^2$ s$^{-1}$), $H$ is the Henry’s law coefficient, $\alpha$ is the accommodation coefficient, and $\bar{c}$ is the average speed of the gas molecules. We can see that $\tau_p$ can vary enormously depending on the Henry’s law coefficient. For $\alpha = 1$ and $T = 298$ K, $\tau_p$ is 0.26 s for the very soluble gas $\text{H}_2\text{O}_2$, $2 \times 10^{-7}$ s for the moderately soluble gas $\text{NH}_3$, and is $6.4 \times 10^{-15}$ s for the insoluble gas $\text{O}_3$. The validity of the equilibrium assumption thus depends on the solubility of the gas.

The next process in the chain of mass transfer is the diffusion of a dissolved species in a drop with a characteristic time of (Seinfeld, 1986, p. 262)

$$\tau_{da} = \frac{r^2}{\pi^2 D_l}. \quad (3.129)$$

The value of $\tau_{da}$ is $10^{-2}$ s, 1 s, and 100 s for drops of 10 µm, 100 µm, and 1 mm in radius, respectively. Note that for drops larger than 100 µm, internal circulation develops and the time scale for which is on the order of $\frac{r \eta_l}{V_\infty \eta_{air}}$ (Seinfeld, 1986, p. 267), where $\eta_l$ and $\eta_{air}$ are the dynamic viscosity of the liquid and air, and $V_\infty$ is the terminal velocity of the drop. Therefore, for both 100 µm and 1 mm size drops, this time scale is on the order of $10^{-2}$ s.

Next, let us consider the ionic dissociation of dissolved species. Usually, the ionization processes achieve equilibria virtually instantaneously (Eigen et al., 1961). For a reversible reaction

$$A \xleftrightarrow[k_r]{k_f} B + C, \quad (3.130)$$

the characteristic time is (Seinfeld, 1986, p. 263)

$$\tau_{ion} = \left\{ k_r + k_f \left( [A] + [B] \right) \right\}^{-1}. \quad (3.131)$$
For example, the dissociation of \( \text{SO}_2 \cdot \text{H}_2\text{O} \) into \( \text{H}^+ \) and \( \text{HSO}_3^- \) at \( \text{pH} = 4 \), \( P_{\text{SO}_2} = 10 \text{ ppb}, \ k_f = 2.4 \times 10^6 \text{ s}^{-1}, \ k_r = 2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \) has a characteristic time of about \( 3 \times 10^{-7} \text{ s} \).

The time scale for the chemical reactions varies according to their specific pathways. Consider the characteristic times for the oxidation of S(IV) by ozone:

\[
\tau_{\text{O}_3} = -\frac{1}{[\text{S(IV)]}} \frac{d[S(IV)]}{dt} = \frac{k_o + \frac{K_{s,1}}{[H^+]}(k_1 + k_2 \frac{K_{s,2}}{[H^+]})}{1 + \frac{K_{s,1}}{[H^+]}(1 + \frac{K_{s,2}}{[H^+]})} [\text{O}_3],
\]

(3.132)

and by hydrogen peroxide:

\[
\tau_{\text{H}_2\text{O}_2} = -\frac{1}{[\text{S(IV)]}} \frac{d[S(IV)]}{dt} = \frac{K_{s,i}k}{\left\{1 + \frac{K_{s,i}}{[H^+]}(1 + \frac{K_{s,2}}{[H^+]})\right\}(1 + K[H^+]}) [\text{H}_2\text{O}_2].
\]

(3.133)

For \( \text{pH} = 4 \) and \( P_{\text{O}_3} = 50 \text{ ppb} \), the time scale for S(IV) oxidation by O\(_3\), \( \tau_{\text{O}_3} \), is about 1300 s; for \( \text{pH} = 4 \) and \( P_{\text{H}_2\text{O}_2} = 1 \text{ ppb} \), the time scale for the oxidation by hydrogen peroxide, \( \tau_{\text{H}_2\text{O}_2} \), is about 1.8 s.

From such analyses, we can see that the mass transfer across the gas-liquid interface for soluble gases and the oxidation of S(IV) both have a time scale near or greater than the time scales of microphysical processes. Therefore, kinetic treatment for these two types of processes is necessary in microphysical models. Equilibrium assumptions can be used for the other processes to simplify the calculations.
3.5.2. **Diffusion of Trace Gases onto Droplets**

1. **Stiff Ordinary Differential Equations**

   The set of ordinary differential equations (ODE’s) for various microphysical and chemical processes that have characteristic times differing by many orders of magnitude is said to be stiff. Solving such stiff ODE’s calls for special attention, especially when the smallest characteristic time is much smaller than the typical model time-step. Classical numerical methods that require time steps smaller than the smallest characteristic times are not adequate for solving the stiff differential equations. Nonclassical methods that take reasonably large time-steps are, therefore, essential for this study. As mentioned in Young and Boris (1977), many nonclassical methods have been applied to reactive flow calculations such as the explicit method, the selected order, multistep predictor-corrector method, the matrix method, and the second-order predictor, iterate-asymptotic corrector scheme (SOPIAC). The last method is used in solving the mass transfer problems in this study.

2. **Second-order Predictor, Iterate-Asymptotic Corrector Scheme**

   Solving microphysical and chemical processes in a multi-phase, multi-component particle system is very different from that for the gas-phase chemical kinetics, which occurs in a single system. There could be thousands of individual aerosol particle systems interacting with each other in a particle framework. This type of framework has the following special features that distinguish the SOPIAC technique from the others. First, the number of dependent variables are so numerous that conventional techniques are not useful. This is especially true for the matrix type methods. Self-starting techniques with low start-stop overhead are preferable. Second, the errors in many microphysical and chemical parameters are generally large so that
there is no need for very high numerical accuracy. Low-order methods are invariably more flexible and run faster. Finally, the problems involved in this type of study are generally very complicated and frequently involve very different schemes. A general integration technique, rather than a highly specialized scheme, is usually superior.

Young and Boris (1977) showed that, for a 1000 s run on a standard 7 species reaction problem, the SOPIAC technique is about 25 times faster than a simple second-order predictor-corrector scheme, 4 to 5 times faster than Kregel’s matrix method, and more efficient than Gear’s method for allowed error percentage greater than $10^{-8}$. With several modifications, some of which come from Easter and Hales (1984), the SOPIAC scheme will be discussed in detail below.

The SOPIAC scheme is essentially a predictor-corrector method that simultaneously solves the ordinary differential equations of the following form:

$$\frac{dy_j}{dt} = g_j - \xi_j y_j \quad , \quad (3.134)$$

where $y_j$ is the concentration of species $j$ at time $t$, $g_j$ the generation rate of species $j$, and $\xi_j$ the first-order rate coefficient for the decay of species $j$. Such an equation set is considered stiff if the time step $\delta t$ is greater than $\tau_j = \frac{1}{\xi_j}$, in which case an asymptotic or an exponentially assisted integration technique is applied. If the equation is not stiff, a conventional predictor-corrector scheme is used. The conventional predictor-corrector equation is in accordance with the improved Euler’s method (Carnahan et al., 1969) which can be expressed as (the subscript $j$ is dropped for convenience)

Predictor: $y_{i+\delta t} = y_i + (g_i - \xi_i y_i)\delta t \quad , \quad (3.135)$

Corrector: $y_{i+\delta t}^m = y_i + (\bar{g}_i - \xi_i \frac{y_i + y_{i+\delta t}^m}{2})\delta t \quad , \quad (3.136)$
where the superscripts denote the number of iterations, whereas $\bar{g}_t$ and $\bar{\xi}_t$ pertain to a simple average over the time interval $dt$:

$$
\bar{g} = \frac{g_t + g_{t+dt}}{2}, \text{ and } \bar{\xi} = \frac{\xi_t + \xi_{t+dt}}{2}.
$$  \tag{3.137}

The generation rate and the decay rate coefficients are thus both averaged over time, which gives better approximation and reduces instability.

However, in dealing with stiff ODE’s, some modifications are necessary for the above method. As shown in Section 2.4.3, equation (3.134) has an analytical solution that is expressed as

\[
y_{t+\delta t} = \frac{g_t}{\xi_t} + \left( y_t - \frac{g_t}{\xi_t} \right) e^{-\xi_t \delta t} = y_t + \frac{\left( g_t - \xi_t y_t \right)(1 - e^{-\xi_t \delta t})}{\bar{\xi}_t},
\]  \tag{3.138}

which can be applied to stiff ODE’s to ensure accuracy and stability. The analytical predictor and corrector expressions are given as

Predictor:  
\[
y^{1}_{t+\delta t} = y_t + \frac{\left( g_t - \xi_t y_t \right)(1 - e^{-\xi_t \delta t})}{\bar{\xi}_t},
\]  \tag{3.139}

Corrector:  
\[
y^{m+1}_{t+\delta t} = y_t + \frac{\left( \bar{g} - \bar{\xi} y_t \right)(1 - e^{-\bar{\xi} \delta t})}{\bar{\xi}},
\]  \tag{3.140}

To avoid time-consuming transcendental functions, asymptotic approximations can be derived by using a few terms of the Taylor’s series expansion to replace $e^{\xi_t \delta t}$ so that

Predictor:  
\[
y^{1}_{t+\delta t} \approx y_t + \frac{\left( g_t - \xi_t y_t \right) \delta t}{1 + \xi_t \delta t},
\]  \tag{3.141}

Corrector:  
\[
y^{m+1}_{t+\delta t} \approx y_t + \frac{\left( \bar{g} - \bar{\xi} y_t \right) \delta t(1 + \bar{\xi} \delta t)}{1 + \bar{\xi} \delta t(1 + \bar{\xi} \delta t/2)}.
\]  \tag{3.142}
In the predictor, only the first-order approximation is used. An additional term is included in the corrector to provide better accuracy and as a practical way of establishing time-step control. The exponential forms (3.139) and (3.140) are considered to be more accurate, especially for true first-order reactions, while the asymptotic forms (3.142) and (3.142) are computationally more efficient and just as reliable as (3.139) and (3.140) for reactions that are not truly first-order. Both the exponential and asymptotic approximations can ensure that the concentrations are always positive. Although requiring more computational time than the improved Euler’s method, it is still advantageous to apply these two approximations on non-stiff equations.

A very important feature of the SOPIAC scheme is the optimization of the time step and the number of iterations. When a stiff equation is close to reaching equilibrium, the change in \( y_j \) over the time step \( \delta t \) is small even though the adjustment time toward equilibrium can be much shorter than the time step. However, when the reaction is far from equilibrium, the time step should be less than the time constant to ensure accuracy. Starting with a small enough time step, the maximum error associated with the calculation in each time step can be used to determine the next time step. The error associated with (3.142) and (3.142) is of the order of \((\delta t)^2\) so that

\[
\varepsilon \sim \alpha (\delta t)^2 \tag{3.143}
\]

where \( \alpha \) is a constant. Analogously, the desired error tolerance \( \varepsilon \) (maximum error allowed) should be proportional to the square of the maximum time-step \((dt_{\text{max}})\) allowed:

\[
\varepsilon \sim \alpha (dt_{\text{max}})^2. \tag{3.144}
\]

The maximum possible time-step can then be taken as the new time-step

\[
\delta t_{\text{new}} = \delta t_{\text{old}} \sqrt{\frac{E}{\varepsilon}} \tag{3.145}
\]
This equation provides a way for time-step control. Under conditions that the scheme fails to converge \((\varepsilon > \bar{\varepsilon})\), the system is restarted with a slightly smaller time step:

\[
\delta t_{\text{old}}^* = f \delta t_{\text{old}}, \quad (3.146)
\]

where \(f\) is normally set to be 0.5. This one half penalty factor \(f\) will be gradually relaxed to unity in succeeding steps.

The number of iterations needed for the corrector depends upon the complexity of the system. Multiple corrector passes provide a mean for enhanced dialogue between equations at the cost of multiplying computational time. As suggested by Easter and Hales (1984), the optimal number of iterations is normally either one or three.

3. Error Relaxation

Under many circumstances the error associated with some specific equations can be large enough to slow down the computation and yet be quite inconsequential to the results. Error relaxation, that can speed up computation significantly, may be applied to the kinetic calculation of chemical processes in the following situations:

1. whenever the concentration becomes negligible,
2. whenever the starting concentration is negligible,
3. whenever the projected concentration is so great as to make the current value and its relative error small by comparison,
4. whenever the projected concentration is negligibly small, and
5. whenever the net rate of change is a small difference of the large generation and decay terms (i.e., the system is very close to reaching equilibrium).

Criteria 1 through 4 were suggested by Easter and Hales (1984). Adjustment must be made, however, according to the type of problem. For example, in particle frameworks, the error in each category may be weighted by their total mass so that time is not wasted on insignificant categories.
The SOPIAC scheme is applied only on the chemical reaction and interfacial mass transfer problems in this study due to several reasons. First, most microphysical processes are non-linear ODE’s, which cause instability and accuracy problems when the linear first-order form (3.134) is applied. Also, microphysical processes are usually more time-consuming than the aqueous-phase chemical reactions. Special schemes, such as those discussed in the previous sections, might be better suited in such situations.

3.5.3. Equilibrium Kinetics

The concentration of a volatile trace gas in the droplets is controlled by the kinetic mass transport across the gas-liquid interface, ionic dissociation, and chemical reactions. All three processes for each droplet must be solved simultaneously for the calculation of the gas- and liquid-phase chemistry. Although the SOPIAC scheme is quite suitable for such purpose, the wide range of characteristic times and large number of equations makes the calculation still very time consuming. However, from the analysis in Section 3.5.1, it is shown that the characteristic times for ionic dissociation are much smaller than all other chemical and microphysical processes. Thus, the ionic dissociation can be considered to reach equilibrium instantaneously within a typical time-step. We can thus reduce the number of equations by combining related ions into a single species. For the reactions considered in this study (see Section 2.4), CO$_2$·H$_2$O, HCO$_3^-$ and CO$_3^{2-}$ are considered as the C(IV) species; NH$_3$·H$_2$O, and NH$_4^+$ are the N(III) species; SO$_2$·H$_2$O, HSO$_3^-$, and SO$_3^{2-}$ are the S(IV) species; and HSO$_4^-$ and SO$_4^{2-}$ are the S(VI) species.
The relationship between the concentration of each ion and that of the total species can be derived from the reaction equations. Take S(IV) as an example. From the reaction equilibrium

$$\text{HSO}_3^- \rightleftharpoons \text{H}^+ + \text{SO}_3^{\approx}$$

we have

$$[\text{HSO}_3^-] = \frac{k_{s2}[\text{SO}_2 \cdot \text{H}_2\text{O}]}{[\text{H}^+]}, \quad [\text{SO}_3^{\approx}] = \frac{k_{s2}[\text{HSO}_3^-]}{[\text{H}^+]^2} = \frac{k_{s1}k_{s2}[\text{SO}_2 \cdot \text{H}_2\text{O}]}{[\text{H}^+]^2}.$$  

(3.148)

The concentration of the S(IV) species is then

$$[\text{S(IV)}] = [\text{SO}_2 \cdot \text{H}_2\text{O}] + [\text{HSO}_3^-] + [\text{SO}_3^{\approx}]$$

$$= \left(1 + \frac{k_{s1}}{[\text{H}^+]} \right) \left(1 + \frac{k_{s2}}{[\text{H}^+]^2}\right) \left[\text{SO}_2 \cdot \text{H}_2\text{O}\right] \equiv \beta_{S(IV)}^*[\text{SO}_2 \cdot \text{H}_2\text{O}],$$

(3.149)

Note that the partial pressure of SO$_2$ in the air under Henry's law equilibrium is

$$P_{\text{SO}_2} = [\text{S(IV)}]/H_{\text{SO}_2} = [\text{SO}_2 \cdot \text{H}_2\text{O}] / (\beta_{S(IV)}^* H_{\text{SO}_2}) = [\text{SO}_2 \cdot \text{H}_2\text{O}] / H_{\text{SO}_2}^*$$

(3.150)

where $H_{\text{SO}_2}^* \equiv H_{\text{SO}_2} \beta_{S(IV)}^*$ is the modified Henry's law coefficient. Similarly, the concentration of the C(IV), N(III), and S(VI) species can be written as

$$[\text{C(IV)}] = [\text{CO}_2 \cdot \text{H}_2\text{O}] + [\text{HCO}_3^-] + [\text{CO}_3^{\approx}] = \left(1 + \frac{k_{c1}}{[\text{H}^+]} \right) \left(1 + \frac{k_{c2}}{[\text{H}^+]^2}\right) [\text{CO}_2 \cdot \text{H}_2\text{O}]$$

$$\equiv \beta_{\text{C(IV)}}^* [\text{CO}_2 \cdot \text{H}_2\text{O}],$$

$$[\text{N(III)}] = [\text{NH}_3 \cdot \text{H}_2\text{O}] + [\text{NH}_4^+] = \left(1 + \frac{k_{a1}}{[\text{OH}^-]}\right) [\text{NH}_3 \cdot \text{H}_2\text{O}]$$

$$\equiv \beta_{\text{N(III)}}^* [\text{NH}_3 \cdot \text{H}_2\text{O}],$$

$$[\text{S(VI)}] = [\text{HSO}_4^-] + [\text{SO}_4^{\approx}] = \left(1 + \frac{k_{s(vi)}}{[\text{H}^+]}\right) [\text{HSO}_4^-].$$

(3.151)
The above simplifications not only reduce the number of equations but also cut down the number of chemical species for each drop category. Note that the variable $y$ in the mass transfer equation (2.183) is actually expressed in terms of the total species concentration, as reflected by the modified Henry's law coefficient in the rate coefficient $\xi$.

The concept of the total species concentration can also be applied to the reaction kinetics. The oxidation of S(IV) by ozone and by hydrogen peroxide can be rewritten as

$$-\frac{d[S(IV)]}{dt} = \frac{k_o + \frac{k_{S1}}{[H^+]}(k_1 + k_2 \frac{k_{S2}}{[H^+]})}{\beta_{S(VI)}}[O_3][S(IV)],$$

$$-\frac{d[S(IV)]}{dt} = \frac{k_{S1}k}{\beta_{S(VI)}(1 + K[H^+])[H_2O_2][S(IV)]},$$

where the reaction constants were defined in Section 2.4.2. Here we have transferred all the rate equations as a function of the concentration of the total species.

The interconnection among the dissolved gases and ions is maintained through the hydronium concentration $[H^+]$. The electroneutrality equation

$$[H^+] + [NH_4^+] = [OH^-] + [HCO_3^-] + 2[CO_3^2-] + [HSO_3^-] + 2[SO_3^-] + [HSO_4^-] + 2[SO_4^2-]$$

(3.153)

can also be written in terms of the total species values:

$$[H^+] + \gamma_{N(III)}[N(III)] = \frac{K_w}{[H^+]} + \gamma_{C(IV)}[C(IV)] + \gamma_{S(IV)}[S(IV)] + \gamma_{S(VI)}[S(VI)],$$

(3.154)

where

$$\gamma_{N(III)} = \frac{k_{Al}[H^+]}{K_w \beta_{N(III)}}, \quad \gamma_{C(IV)} = \frac{k_{Cl}(1 + 2k_{C2})}{\beta_{C(IV)}},$$
These γ's represent the ability of dissolved gases to produce ions, and have values of γ_{N(III)} \sim 1, \gamma_{C(IV)} \sim 0, \gamma_{S(IV)} \sim 0.8 and \gamma_{S(VI)} \sim 1.8 in cloud drops with pH \sim 3. For example, a γ_{S(IV)} \sim 0.8 means that about 80% of the dissolved S(IV) exists in the form of bisulfite and only 20% exist as dissolved SO_2. Since γ and β^* are functions of [H^+] , equation (3.151) can be solved for [H^+] by iteration.

Because of their common dependence on the [H^+], the mass transfer equations and the electroneutrality equation have to be solved simultaneously. However, doing such iteration within the modified Euler's method, which is also an iteration scheme, is sometimes very time consuming. We can alternatively transform (3.151) into a finite difference form and solve it together with the mass transfer equations by applying the advanced finite-difference schemes. By scale analysis, one can find that the changes of γ under normal pH are always much smaller than the change of [H^+]. The coefficient γ for each species can be regarded as constant for a small change of [H^+]. Therefore, by taking the derivative of equation (3.151), the pseudo-reaction rate of [H^+] can be expressed in terms of the rate changes of other trace species:

\[
\frac{d[H^+]}{dt} = -\frac{\gamma_{N(III)}d[N(III)] + \gamma_{C(IV)}d[C(IV)] + \gamma_{S(IV)}d[S(IV)] + \gamma_{S(VI)}d[S(VI)]}{1 + \frac{K_w}{[H^+]^2}}.
\]

(3.155)

The error associated with the pseudo-reaction rate is always much less than the percentage change of [H^+] during one time step.
3.6. Lookup Tables

Many of the microphysical parameters, such as the collision efficiencies, are very complicated functions that require extensive computation. It is common to parameterize these variables as functions of a limited number of variables from experimentally or theoretically determined data to save computational time. However, there are times that the experimentally or theoretically determined data set can only be expressed in complicated forms, which still require substantial computational time. Also, a carelessly formulated parameterization scheme can give erroneous values, especially when the values are extrapolated beyond the range of the original data set. For instance, Lee (1990) derived an empirical formula for the drop collision based on the data of Shafrir and Neiburger (1963) and other sources. It is found that his formula may give negative values for collector drop size larger than 136 $\mu$m -- the upper limit of the original data set. Alternatively, we can calculate the intended parameters in advance and interpolate them into evenly spaced grid points for easy access. We call the predetermined data sets the *lookup tables*. The integrity of the *lookup tables* can be checked before the simulations. Such a process needs to be done only once. One can then access these tables to find a desired value with minimal computational time. While accessing the lookup tables one may use interpolation schemes to find a specific value. In cases that the grid intervals of the lookup table are small compare with the accuracy of the original data, one can simply use a fixed value for each grid interval. Besides saving computational time, the lookup tables can also be used to facilitate the bin methods. As discussed in Section 3.1, one needs to know the functional form of the growth kernels to do the method-of-moments type calculation. One may use the lookup table concept to get a first-order approximation for the growth kernel within individual grid intervals.
The drop collision efficiencies have been investigated both numerically and experimentally for decades. The results from the numerical studies provide more detailed information than the experimental results and are more suitable to be used in this study. Among the numerous numerical studies, de Almeida (1979) included the effects of small-scale turbulent motions and provided tables for the collision efficiency values at three different rates of energy dissipation. Figures 3.20 to 3.22 show de Almeida's collision efficiencies as a function of the Reynolds number of the large drop and the ratio of small-drop size to large-drop size, which is used is this study. Note that the original tables use the large-drop size as the first table-variable instead of the Reynolds number. However, the collision efficiencies also vary with air pressure. By using the Reynolds number, the pressure effect is at least partially included. The calculation of the drop Reynolds numbers and fall-velocities follows Pruppacher and Klett (1980, pp. 322-328).

Figure 3.20: Collision efficiencies as a function of the large-drop size $r_1$ and the ratio of the two drop-sizes $r_2 / r_1$ for rate of energy dissipation $e = 0 \text{ cm}^2 \text{ s}^{-3}$. 
Figure 3.21: Same as Figure 3.20 except for $e = 1 \text{ cm}^2 \text{ s}^{-3}$.

Figure 3.22: Same as Figure 3.20 except for $e = 10 \text{ cm}^2 \text{ s}^{-3}$.
3.6.2. Lookup Tables for the Breakup Distribution Functions

The breakup distribution functions of Low and List (1982b) discussed in Section 2.2.3.2 are very complicated and computationally extensive. It would be most beneficial to use lookup tables for parameters of this kind. Following the formulas in Section 2.2.3.2, we can calculate the number distribution for the breakup droplets, \( N(D_X; D_L, D_S) \), as a function of the diameter of the fragment drops \( D_X \), and the large parent drop \( D_L \), and small parent drop \( D_S \). The stereo-graph shown in Section 2.2.3.2 is an example of a slice in the three-dimensional lookup table. In order to conserve both number and mass, a second table for the mass distribution \( M(D_X; D_L, D_S) \) is needed. Since the bin resolution used here is rather fine (bin sizing factor of 1.3 to 2 at the size range of interest) and the accuracy of Low and List's formulas is not particularly high, we can simply use the value given in the table for each bin without interpolation.

We also need a third lookup table to account for the redistribution of solute. This lookup table contains four parameters \( Q_{L,S}, Q_{L,X}, Q_{S,L}, \) and \( Q_{S,X} \) for each pair of parent drops. The parameters \( Q_{i,j} \) represent the fraction of mass of the parent drop \( i \) that is lost to the other parent drop or to the fragment drops \( j \). The subscripts \( L, S, \) and \( X \) represent the large, small, and fragment drops, respectively. From these water-mass fractions, one can calculate the redistribution of solute among all the breakup droplets.
3.6.3. Lookup Tables for the Ice-drop Collision Efficiencies

Both the experimental and theoretical studies on the collision efficiencies between ice crystals and droplets are rather scarce. Schlamp et al. (1975) computed the collision efficiencies for columnar ice collecting small drops, while Lew and Pruppacher (1983) gave that for large drops collecting small columnar ice. Pitter and Pruppacher (1974), as well as Pitter (1977), provided the collision efficiency for planar ice collecting small drops, while Lew et al. (1985) provided that for large drops collecting small planar ice. Lookup tables for the collision efficiencies between ice particles and drops are constructed from the above sources. However, there are some modifications needed.

The data sets for ice and drop as collectors are combined to give a full set of size ranges. Yet, there is not enough information to cover the whole size ranges. We need to fill in the gaps. One may observe that the collision efficiency reaches a minimum when the drop being collected reaches a size such that its fall velocity approaches that of the collector ice particle. For drops of even larger sizes, the relative velocity between drop and ice crystal changes sign and the collision efficiency increases again. A mirror image about the minimum of the collision efficiencies can be assumed so that interpolations can be made between existing data. For a collector-drop size larger than that given by Lew and Pruppacher (1983) and Lew et al. (1985), the collision efficiencies remain virtually unchanged and can be assumed to be constant for a fixed ice-crystal size. The resulting full pictures of the collision efficiencies are demonstrated in Figures 3.23 and 3.24. The original data sets are transformed into matrixes with drop and ice crystal axes expressed in terms of log Reynolds numbers. The calculation of the Reynolds number and the fall velocity of ice particles follows the approach of Böhm (1989).
The existing data for the collision efficiencies gave only qualitative descriptions about the ice crystal shape (either planar or columnar). In order to include the shape effect, an aspect ratio of 0.1 is assumed for the planar ice and 10 is assumed for the columnar ice. The data set for drop-drop interactions is borrowed to represent spherical ice-drop collision efficiencies (aspect ratio = 1). Interpolation or extrapolation then can be made using these three data sets. One should recognize, however, that the tables for ice-drop collision efficiencies introduced here are far from perfect.
Figure 3.23: Collision efficiency between planar ice crystals and drops as a function of the particles Reynolds number.

Figure 3.24: Same as Figure 3.23 except for columnar ice and droplets.
3.7. Miscellaneous Numerical Methods

3.7.1. Operator Splitting

Similar to the staggering of spatial grids that are frequently used in dynamic models (e.g., Lilly, 1961), one can also use the time splitting technique to stagger processes in time. This time-splitting technique is used not only in dynamic models but also in cloud models. For example, Easter and Hales (1984) applied the operator splitting technique so that the time steps used for dynamic transport do not have to match the smaller time step that is necessary for the microphysics or chemistry. The same concept can be used to separate different microphysical and chemical processes. For example, we can use a smaller time-step for the condensation process while using a larger time-step for the hydrodynamic interactions.

Not only can we use different time-steps for different processes, it is also advantageous to stagger these processes in time. For instance, one can execute process A for a time of $\delta t/2$, then process B for $\delta t$, and back to process A for another $\delta t/2$. By doing this, both processes are using the "mean" results from the other. This time staggering can be used in combination with the operator splitting technique so that, during the $\delta t/2$ time for process A, the calculation is executed n times with a time step of $\delta t/(2n)$. 
3.7.2. Variable Time Step

The minimum time step required in numerical simulations depends not only on the type of process but also on the time-stages in a particular process. Thus, a numerical technique that allows variable time steps is very important to the computational efficiency. The largest change of the required time step for a single microphysical process occurs probably during the activation stage of the condensation growth. Árnason and Brown (1971) used eigenvalues as a stability criterion for determining the time step in solving the differential equations for condensational growth. Hagen (1979), on the other hand, use the nonlinearity of the air pressure to control the time step. Clark (1973) utilized the "saturation equation" to determine the time scale of the saturation ratio and used it as the criterion for the computational time step. However, a large error would result during the activation stage. The error occurs because the above methods check mainly the nonlinearity of the gas-phase properties such as saturation ratio, pressure, or temperature, but not the nonlinearity of the growth of individual droplets. The analytical solution for condensational growth introduced in Section 3.3 greatly relaxed the maximum time step. However, a scheme that can determine an optimal time step might still be necessary in other situations. As mentioned in Section 3.5.2, the time-steps used in the predictor-corrector method can be determined by limiting the maximum allowed error during each iteration. One can adopt such error-checking scheme to determine the time step required in any process. Another scheme that can be used to determine the time step is the forecasting method discussed in Section 3.2.1. One can determine the time steps by limiting the difference between the forecasted and the computed results. Note that it is not easy to find a generalized method for various processes. One may need to apply more than one method to determine the time step.
3.7.3. **Pointers for Reducing Dimensions**

There is one major difference between the particle framework and the spatial framework: the bins of the particle framework could be empty. In subsaturated air, particles exist in their haze state and have a very small amount of liquid water. Therefore, bins that represents high water-mass will not contain any particles. Even after the cloud is formed, the cloud drop spectrum is still quite narrow before drops start to coalesce. Generally speaking, more than two-thirds of the bins are constantly empty. Making calculation for the empty bins not only costs computational time, but it also take unnecessary memory storage. We can, therefore, store only the filled bins and apply a pointer array that contains the bin identification information. Such a pointer array only has to be created once in each time step, but it can be used for all of the process modules.

3.8. **Summary**

The multi-dimension particle frameworks are the vital part of the numerical method for this study. Only a couple of existing cloud models (Chen and Lamb, 1992a; Roelof, 1992) are capable of resolving the particle spectra in more than one component. The hybrid bin method, a method-of-moment type scheme, is an essential technique for applying the particle framework to various cloud microphysical and chemical processes. Various specialized numerical techniques have also been introduced in this chapter to solve the differential equations for the various microphysical and chemical processes. These numerical methods, while not necessarily the best of their kind, are nevertheless very useful to the numerical simulation of cloud processes.
Chapter 4

SIMULATIONS

The detailed microphysical processes responsible for cloud and precipitation formation control the efficiencies with which water vapor and trace chemicals are removed from the atmosphere. At the earlier stage of this study (Lamb and Chen, 1988; Lamb and Chen, 1990), it was found that specific microphysical processes responsible for the growth of cloud and precipitation also lead to chemical fractionation and removal efficiencies that can vary by orders of magnitude. The concept of relative removal efficiency (the ratio of the trace chemical to water vapor removal efficiencies), which relate directly to the chemical and microphysical parameters, is useful in the parameterization of the wet removal of trace chemicals. Such a concept was applied in a simple particle-tracing model, which incorporated some laboratory results of ice-phase chemistry, as will be shown in Section 4.1. The absolute amount of the wet removal, however, is directly controlled by the detailed microphysical processes. A multi-component microphysical model is therefore developed to provide detailed description of the microphysical processes. Section 4.2 is also a published article (Chen and Lamb, 1992a), which describes liquid-phase part of the multi-component model. Ice-phase microphysics is included in the Chen and Lamb (1992b) paper, as will be shown in Section 4.3. The model with complete microphysics and chemistry is applied in a two-dimensional steady-state model to simulate an orographic cloud. The results from this final simulation are given in Section 4.4.
4.1. The Role of Precipitation Microphysics in the Selective Filtration of Air Entering the Upper Troposphere

The material in this section is adapted from a paper published in the Preprints, Conference on Cloud Physics, San Francisco, CA, July 23-27, 1990, pp. 479-484.

4.1.1. Introduction

The removal of atmospheric trace substances by cloud processes is very important in determining their long range transport and deposition patterns. The microphysics of precipitation formation, in particular, leads to chemical fractionation and to an effective, species-dependent filtration of the air passing through the cloud system that helps control the global budgets of many trace substances, including water vapor. Due to their relatively small scales and short life times, however, clouds often represent subgrid-scale and transient phenomena that can not be explicitly simulated in large scale or climate models. Simple parameterizations are, therefore, necessary in calculating the wet removal processes.

Owing to a lack of knowledge about ice-phase microphysics and chemistry, parameterizations for trace-chemical removal by precipitation have been developed primarily for aqueous-phase, warm-cloud processes. While some have assumed that all the precipitation is in the liquid-phase (Giorgi and Chameides, 1986; Walcek and Taylor, 1986; Tremblly and Leighton, 1986; and Niewiadomski, 1989), others that included ice condensate in their models ignored the ice-phase chemistry (Chang et al., 1987; and Taylor, 1989). Easter and Luecken (1988) included the absorption of HNO₃ onto snow and graupel but neglected other trace gases. Cho et al. (1989) compared a simulation that retained all solute in the ice-phase with a simulation that allowed no solute in the
solid-phase as liquid drops froze during the formation of precipitation. They showed that, without including complicated ice-phase chemistry, there were differences of up to 37% in the total sulfate deposition. Such differences are substantial and should affect the results of any model that claims to be quantitative.

Lamb and Blumenstein (1987) and Iribarne and Pyshnov (1988) (LB and IP hereafter) studied the amount of solute retained as cloud drops freeze during riming; Clapsaddle and Lamb (1989) and Valdez et al. (1989) (CL and VDB hereafter) studied the sorption of trace gases onto ice. As new experimental results on the ice-phase microphysics and chemistry become available, it is possible to develop realistic parameterizations of the effects of ice-phase precipitation.

More sophisticated treatments of wet removal would substantially increase the computation time of multi-dimension models, so it is necessary to derive simple parameterizations for the ice-phase chemistry and microphysics. Giorgi and Chameides (1985) used a first-order rainout parameterization in a photochemical model. They related the rainout frequencies of trace species to that of water through the solubility of the trace species which can be readily calculated. This concept is similar to the concept of relative removal efficiency developed by Lamb and Chen (1990). This paper extends these ideas further and introduces additional parameterizations of ice-phase chemistry developed from recent laboratory investigations.
4.1.2. Rainout Frequencies and the Relative Removal Efficiencies

The first-order parameterization of the rate of wet removal (Giorgi and Chameides, 1985) for a trace species j at altitude z can be expressed as

\[ W_j(z) = n_j(z) k_j(z), \quad (4.1) \]

where \( n_j(z) \) and \( k_j(z) \) are the species concentration in the air and the rainout frequency at altitude z, respectively. In order to calculate the rate of wet removal, the rainout frequency must be obtained from either an observational or a theoretical approach. To obtain the rainout frequency for each trace species through observation is not a practical method due to its uncertainties and technical difficulties. Since water serves as the host of trace species in the precipitation, it is quite feasible to relate the rainout frequency of a trace species to its solubility in water and the rainout frequency of water. In addition, the rainout frequency of water is usually a trackable parameter in most atmospheric models. Therefore, the solubility of the trace species can be used to parameterize the rate of wet removal.

Since most of the trace species exist in the precipitation via dissolution into the condensate, the ratio of the wet removal rates of two species equals the ratio of their concentrations in the precipitation. By choosing water as the reference species and omitting the altitude subscript, the relationship can be expressed as

\[ \frac{W_j}{W_{H_2O}} = \frac{[j]}{[H_2O]}, \quad (4.2) \]

where \([j]\) is the concentration of species j in the precipitation, and \([H_2O]\) is the concentration of water in the precipitation, which is approximately constant. From (4.1) and (4.2), the ratio of the rainout frequencies between a species j and water is

\[ \frac{k_j}{k_{H_2O}} = \frac{[j]/n_j}{[H_2O]/n_{H_2O}}, \quad (4.3) \]
which equals the ratio of the two removal efficiencies between species $j$ and water. This ratio is identical to the relative removal efficiency $\varepsilon_j$ defined by Lamb and Chen (1990), as well as to the normalized scavenging ratio of Englemann (1988). Note that both $n_j$ and $n_{H_2O}$ are trackable parameters, and only $[j]$ needs be known to calculate the relative removal efficiency. From Henry’s Law,

$$[j] = n_j^\text{eq} H_j^* R T,$$  \hspace{1cm} (4.4)

where $n_j^\text{eq}$ is the equilibrium species concentration in the air, $H_j^*$ is the overall Henry’s Law solubility coefficient, $R$ is the gas constant, and $T$ is the temperature. So, the total species concentration in the cloudy air is

$$n_j = n_j^\text{eq} + [j] v_{liq}$$  \hspace{1cm} (4.5)

where $v_{liq}$ is the volume of liquid water per unit volume of air. Thus, the liquid-phase concentration can be derived from (4.4) and (4.5):

$$[j] = \frac{n_j H_j^* R T}{1 + H_j^* R T v_{liq}}.$$  \hspace{1cm} (4.6)

The relative removal efficiency is thus

$$\varepsilon_j = \frac{n_{H_2O}}{[H_2O]} \frac{H_j^* R T}{1 + H_j^* R T v_{liq}},$$  \hspace{1cm} (4.7)

which can be determined by the total water and liquid water content in the air and the solubility of the species. Then, the species rainout frequency exhibits a simple proportionality to that of water:

$$k_j = k_{H_2O} \varepsilon_j.$$  \hspace{1cm} (4.8)

Note: Giorgi and Chameides (1985) considered the transient effects of clouds and pointed out that the time-averaged wet removal rate $\{W_j\}$ does not equal the product of the time-averaged species concentration $\{n_j\}$ and the rainout frequency $\{k_j\}$. 

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Modification due to the transient effects can be made by assuming that the species concentration in the air is constant during the dry period, but a function of time during the wet period. In order to calculate the aqueous-phase concentration from (6) with this approach, however, a species concentration in the air during the dry period should be used instead of the time-averaged concentration for the whole precipitation cycle.

4.1.3. Ice-Phase Parameterizations

The parameterizations given in the last section can be extended to include the ice-phase processes. There are basically two types of ice growth processes: (1) the accretion of supercooled liquid water (riming) and (2) vapor deposition onto ice. Iribarne et al. (1983), LB, and IP showed that not of all the originally dissolved gases would be expelled from the freezing liquid during riming. A significant amount of volatile trace species previously in heterogeneous equilibrium with the liquid phase is actually trapped within the ice. For the depositional process, trace gases can be scavenged significantly by falling snow through adsorption processes. CL explored the sorption behavior of SO$_2$ on ice that was in equilibrium with the environmental water vapor. VDB studied the incorporation of SO$_2$ into bulk ice during depositional growth. These experiments show that the concentration of trace species in the condensate depends on the temperature and the type of condensate. If temperature and the type of condensate are the major independent variables for the concentration of trace chemicals in the condensate, it would be most convenient to separate the parameterization for wet removal into chemical parameters and microphysical parameters since chemical variables generally do not influence the dynamics and microphysics of the cloud (Cho et al., 1989).
If the precipitation is partitioned into liquid water, rime ice, and depositional ice, the relative removal efficiency $\varepsilon_j$ of species $j$ can be generalized as

$$
\varepsilon_j = \varepsilon_{j,\text{liq}} q_{\text{liq}} + \varepsilon_{j,\text{rim}} q_{\text{rim}} + \varepsilon_{j,\text{dep}} q_{\text{dep}},
$$

(4.9)

where $q$ is the mass fraction of the total condensate, and the subscripts 'liq', 'rim', and 'dep' represent the liquid water, rime ice, and the depositional ice, respectively. The total relative removal efficiency is, then, the sum of the individual relative removal efficiencies for each type of condensate. The mass balance equation (5) can also be generalized as

$$
n_j = n_{j,\text{liq}} + [j]_{\text{liq}} v_{\text{liq}} + [j]_{\text{rim}} v_{\text{rim}} + [j]_{\text{dep}} v_{\text{dep}},
$$

(4.10)

where $[j]_{\text{liq}}$, $[j]_{\text{rim}}$, and $[j]_{\text{dep}}$ are the species concentration and $v_{\text{liq}}$, $v_{\text{rim}}$, and $v_{\text{dep}}$ are the volume of each of the condensate forms per unit volume of air. The terms on the right hand side represent the amount of species $j$ in the interstitial air, liquid water, rime ice, and depositional ice. Note that $q_{\text{liq}}$, $q_{\text{rim}}$, and $q_{\text{dep}}$ in (4.9) are equal to the ratio of $v_{\text{liq}}$, $v_{\text{rim}}$, and $v_{\text{dep}}$ to the total volume concentration of the condensate $v_t$.

The species concentration in the liquid water is determined from the Henry's Law equilibrium:

$$
[j]_{\text{liq}} = n_j^{\text{eq}} H_j^* R T.
$$

(4.11)

Applying the concept of the entrapment factor as in LB, we note that the species concentration in the rime ice is

$$
[j]_{\text{rim}} = f_{j,\text{ent}} [j]_{\text{liq}},
$$

(4.12)

where $f_{j,\text{ent}}$ is the entrapment factor for species $j$. From CL and VDB's experiments, the species concentration in the depositional ice is related to that in the air through an equilibrium relationship similar to that for the liquid phase:
\[ [j]_{\text{dep}} = n_j \text{^eq}_j H^*_j R T, \quad (4.13) \]

where \( H^*_j \) is an analogous overall Henry's Law solubility coefficient for trace gases incorporated into ice by sorption processes. Defining a \textit{sorption factor} as

\[ f_{j,sor} = \frac{H^*_j}{H^*_j} \quad (4.14) \]

and applying (4.11) and (4.13), we can express \([j]_{\text{dep}}\) in a form similar to that for \([j]_{\text{rim}}\) as in (4.12):

\[ [j]_{\text{dep}} = f_{j,sor} [j]_{\text{liq}} \quad (4.13a) \]

The species concentration in the liquid \([j]_{\text{liq}}\) can be solved by inserting (4.11), (4.12), and (4.13a) into (4.10):

\[ [j]_{\text{liq}} = \frac{n_j H^*_j R T}{1 + A} \quad (4.15) \]

where

\[ A = (q_{\text{liq}} + f_{j,\text{ent}} q_{\text{rim}} + f_{j,sor} q_{\text{dep}}) \frac{H^*_j R T v_i}{q^* H^*_j R T v_t} \]

and \( q^* \) is a modification factor for the all-liquid type of parameterization when mixed-phase cloud processes are considered. Equation (4.15) is essentially a generalized form of (6) for the species concentration in the total condensate. The species concentrations in the ice-phase condensates can then be obtained by replacing (4.15) back into (4.12), and (4.13a).

The generalized relative removal efficiency of species \( j \) in the liquid condensate is now

\[ \epsilon_{j,\text{liq}} = \frac{[j]_{\text{liq}} / n_j}{[H_2O] / n_{H_2O}} = \frac{n_{H_2O}}{n_{H_2O}} \cdot \frac{H^*_j R T}{1 + q^* H^*_j R T v_t}, \quad (4.16) \]

and the overall relative removal efficiency is

\[ \epsilon_j = \epsilon_{j,\text{liq}} (q_{\text{liq}} + f_{j,\text{ent}} q_{\text{rim}} + f_{j,sor} q_{\text{dep}}) = \epsilon_{j,\text{liq}} q^*. \quad (4.17) \]
This means that the relative removal efficiency and, therefore, the rainout frequency calculated using aqueous-phase Henry's Law equilibrium should be modified by the factor $q^*$ to include ice-phase chemistry. Note that if the precipitation is all in the liquid-phase ($q^* = q_{\text{liq}} = 1$, $v_t = v_{\text{liq}}$), equations (4.15) and (4.17) reduce to (4.6) and (4.7).

The parameterization for the wet removal of trace chemicals is now separated into (1) the microphysical parameters: $q_{\text{liq}}$, $q_{\text{rim}}$, and $q_{\text{dep}}$; and (2) the chemical parameters: $H_j^*$, $f_{j,\text{ent}}$, and $f_{j,\text{sor}}$. The chemical parameters are basically functions of temperature and pH, and are generally obtained from laboratory experimentation. More details about the chemical parameters will be discussed in the next section. The microphysical parameters depend primarily on the physical and environmental properties of the cloud. Walcek and Taylor (1986) used an empirical fit to the observed liquid water mixing ratio (from Warner, 1970) which would be observed were a parcel to rise adiabatically from cloud base. They, however, did not consider the possible presence of the ice-phase. To a first approximation, the fraction of liquid water in the total condensate varies from unity at the 0°C level to zero at about -40°C. Chang et al. (1987) used the same empirical fit as in Walcek and Taylor for the condensed water content and, in addition, accounted for the ice phase by letting the ice fraction vary linearly with temperature to an all-ice threshold of -18°C. To further partition the ice phase, the fraction of rime ice to the total ice can be considered to have a similar temperature variation since the degree of riming is proportional to the amount of liquid water. In reality, however, it is difficult to make such a simple quantitative description about the rime ice fraction due to the very complex microphysical nature of the growth processes. Realistic parameterizations for the condensed water contents may be derived more appropriately from a detailed microphysical model.
4.1.4. The Chemical Parameters

The Henry's Law coefficients for most atmospheric trace gases interacting with water have been experimentally determined and, therefore, the parameter $H_j^*$ can be calculated quite easily. IP showed that for species, such as HCl, HNO$_3$, NH$_3$, and H$_2$O$_2$ in the liquid, the dissolved gases are totally retained by the ice ($f_{j,\text{ent}} = 1$) during riming. Their experiments on SO$_2$ showed that about half of the S(IV) contained in droplets remain in the ice after freezing, with a slight temperature dependence to the "retention coefficient". LB, however, showed the fraction of S(IV) entrapped by the riming process is proportional to the drop supercooling $\Delta T$ and varies from about 14% at -20 °C to about 1% at 0 °C. From a regression analysis, their entrapment factor is expressed as

$$f_{S(IV),\text{ent}} = a \Delta T + b,$$

where $a = (5.8\pm0.5) \times 10^{-3}$ K$^{-1}$ and $b = (1.2\pm0.6) \times 10^{-2}$. A comparison of different parameterizations for the entrapment factor applied in model calculations can be found in Lamb and Chen (1990).

VDB studied the incorporation of SO$_2$ into ice deposited from the vapor at -15 °C and found that SO$_2$ was captured in deposited ice at concentrations comparable to the equilibrium SO$_2$ concentration in the aqueous-phase at 0 °C. The S(IV) concentration in the liquid can be expressed as

$$[S(IV)]_{\text{liq}} = [SO_2\cdot H_2O] + [HSO_3^-] + [SO_4^{2-}] .$$

(4.19)

For normal atmospheric pH values of 3 to 6, most S(IV) exists as [HSO$_3$] in the liquid and the total S(IV) is approximately (Barrie, 1978)

$$[S(IV)]_{\text{liq}} \approx (H_s K_{s1} P_{SO_2})^{1/2} ,$$

(4.19a)
where $H_s$ is the Henry's Law coefficient, $K_{s1}$ is the first dissociation coefficient, and $P_{SO_2}$ is the partial pressure of $SO_2$. From the van't Hoff equation, $H_s$ and $K_{s1}$ can be expressed in the Arrhenius forms:

$$ H_s = H_s^o \exp\left(-\frac{\Delta H_{H_s}}{RT}\right), \quad (4.20) $$

$$ K_{s1} = K_{s1}^o \exp\left(-\frac{\Delta H_{K_{s1}}}{RT}\right), \quad (4.21) $$

where $H_s^o = 3.013 \times 10^{-5} \text{ M atm}^{-1}$, $K_{s1}^o = 1.827 \times 10^{-5} \text{ M atm}^{-1}$; $\Delta H_{H_s} = -2.634 \times 10^4 \text{ J mol}^{-1}$, and $\Delta H_{K_{s1}} = -1.633 \times 10^4 \text{ J mol}^{-1}$ are the changes of enthalpy due to dissolution and dissociation (from Maahs, 1982). The concentration of $S(IV)$ sorbed in the ice, according to VDB, is then:

$$ [S(IV)]_{dep} = \sqrt{H_s^o K_{s1}^o \exp\left(-\frac{\Delta H_{H_s} + \Delta H_{K_{s1}}}{2RT_o}\right) P_{SO_2}^{1/2}}, \quad (4.22) $$

where $T_o = 273.15 \text{ K}$. The sorption factor for $SO_2$ can now be expressed as

$$ f_{S(IV),sor} = \frac{[S(IV)]_{dep}}{[S(IV)]_{liq}} = \alpha \exp\left(\frac{\beta}{T}\right), \quad (4.23) $$

where

$$ \alpha = \exp\left(-\frac{\Delta H_{H_s} + \Delta H_{K_{s1}}}{2RT_o}\right) = 1.202 \times 10^4, $$

and

$$ \beta = \frac{\Delta H_{H_s} + \Delta H_{K_{s1}}}{2RT} = -2.566 \times 10^3 \text{ K}. $$

Note that $f_{S(IV),sor}$ does not depend on the pH or $P_{SO_2}$ and is a function of temperature only when the approximation of (4.19a) is used.
While VDB studied the sorption process for ice actively growing by vapor deposition, CL measured the sorption of SO$_2$ on ice which was in equilibrium with the environmental water vapor at different temperatures. They showed that the S(IV) concentration in ice is almost proportional to the square root of $P_{SO_2}$ (Clapsaddle, 1989) and is a function of temperature. From their data, the S(IV) concentration in ice can be expressed as

$$[\text{S(IV)}]_{\text{dep}} = c \exp\left(\frac{d}{T}\right)P_{SO_2}^{1/2},$$

where $c = 8.0 \times 10^{-8}$ M atm$^{-1/2}$ and $d = -6.06 \times 10^{-5}$ K. The sorption factor in this case should then be:

$$f_{\text{S(IV), sor}} = \frac{[\text{S(IV)}]_{\text{dep}}}{[\text{S(IV)}]_{\text{liq}}} = \alpha' \exp\left(\frac{\beta'}{T}\right),$$

where $\alpha' = 3.41 \times 10^{13}$ and $\beta' = -8.627 \times 10^{3}$ K. By either parameterization, equation (4.23) or (4.25), the sorption factor for SO$_2$ is a function of temperature only.

It was not determined in the results of CL, however, whether the SO$_2$ existed in the bulk ice or only on the surface under the equilibrium conditions. Should this result be interpreted as a surface sorption process, the S(IV) concentration on the surface could be approximated by

$$[\text{S(IV)}]_{\text{dep}}^{\text{surf}} = c' \exp\left(\frac{d'}{T}\right)P_{SO_2}^{1/2},$$

where $c' = 8.5 \times 10^{5}$ mol m$^{-2}$ and $d' = -2.272 \times 10^{3}$ K. But the sorption factor now depends on the microphysics (surface area of all ice particles) and is, therefore, more difficult to apply. From the results of VDB, however, it is probably safe to assume that the sorption process is a bulk phenomenon, at least under the growth situations. Besides HNO$_3$ (Huebert et al., 1982), the sorption processes of trace gases other than SO$_2$ on ice are not well known and require further laboratory study.
4.1.5. Precipitation Growth Model

A conceptually simple model is used here to simulate the acquisition of trace chemicals by ice-phase precipitation elements falling through a background cloud. The background cloud is parameterized by letting a Lagrangian air parcel ascend adiabatically to form a steady-state vertical profile with the following properties: H$_2$O, CO$_2$, NH$_3$, and SO$_2$ mixing ratios of 5 g kg$^{-1}$, 332 ppmv, 0.5 ppbv, and 10 ppbv, respectively; surface temperature of 10 °C, and pressure of 1000 mb; the fraction of the total condensate that exists as ice varies linearly from zero at 0 °C to unity at -40 °C. Energy and mass are conserved, and chemical equilibrium are maintained between the gaseous species and the liquid drops throughout the depth. An ice embryo 100 µm in radius is introduced into the background cloud at the -30 °C level and allowed to grow by hydrodynamic collection and vapor deposition while falling at its terminal velocity. (More detailed description of the model development can be found in Lamb and Chen, 1990). The entrapment factor in (4.18) is used for the acquisition of S(IV) through riming, and three parameterizations of SO$_2$ sorption are employed for the depositional growth of the ice particle.

The growth of the ice particle in water mass and the simultaneous acquisition of trace chemicals can be presented differentially or cumulatively. Figure 4.1 demonstrates the variation of the S(IV) concentrations (left axis) and relative removal efficiencies (right axis) of the ice particle in a differential form. Each layer of the ice particle (top axis) represents the environmental condition at each background-cloud level (bottom axis) that the particle experienced during its growth. Note that the relative removal efficiency (R.R.E.) is directly proportional to the condensed-phase concentration for a given air parcel at different altitudes. Curves A and C are the S(IV) concentration in the depositional ice calculated using the empirical formulae (4.22) from VDB, and (4.24)
from \text{CL}, respectively. Curve A shows an exponential (linear on a log scale) increase of the S(IV) concentration with temperature as (4.24) indicated. There is actually no temperature dependence, as shown in (4.22), for curve C. The indicated variation reflected the fact that the partial pressure of SO₂ decreases with increasing altitude and, therefore, decreasing temperature. Curve B shows the entrapment of S(IV) during riming, using the entrapment factor from \text{LB}. Curve D shows what the S(IV) concentration would be in the cloud drops if no NH₃ and CO₂ were present. Since no interaction with other trace chemicals is considered, the S(IV) concentration in ice due to sorption using the parameterization from \text{VDB} should equal the concentration in the liquid in equilibrium with pure SO₂ environment at 0°C (indicated by the intersection of curves C and D at 0°C).

In general, the R.R.E. of S(IV) in the liquid (curve E) is near unity, which means that S(IV) can be removed almost as effectively as water by aqueous-phase precipitation. The R.R.E. of S(IV) in ice is about one half to more than two orders of magnitude smaller than that in the liquid. Note that there is a substantial difference between the RRE using the parameterization from \text{CL} and that from \text{VDB}, especially at lower temperatures. The R.R.E. for entrapment (\text{LB}) is in a similar range as the R.R.E. for sorption (\text{CL}) with an opposite temperature dependence. The sorption process seems to be more effective than the entrapment process at higher temperatures, and less effective at lower temperatures. It will be shown later, however, that the microphysical processes (vapor deposition and riming) have an opposite trend. The two chemical parameters, the sorption factor and the entrapment factor, are manifested by the ratio of curves A to E, and the ratio of B to E, respectively.

As the differential form is used to represent different cloud levels, so a cumulative form can be used to represent the relative removal efficiency for the whole...
Figure 4.1: Differential S(IV) concentrations (left axis) and relative removal efficiencies (R.R.E., right axis) for different condensate-types at various layers of the ice particles (top axis) and various temperature levels of the background cloud (bottom axis): A: sorption (from CL) in the depositional ice; B: entrapment (from LB) in the rime ice; C: sorption (from VDB) in the depositional ice; D: sorption in the liquid-water that is in equilibrium with a SO₂-only environment; and E: sorption in the background cloud-drops.
cloud. In addition to the chemical parameters applied in the differential presentation, the microphysical parameters ($Q_{\text{dep}}$ and $Q_{\text{rim}}$) are also needed in the cumulative concept. The microphysical parameter considered here is the rime fraction, which is the mass fraction of rime ice in the total ice as shown by the thin solid-line in Figure 4.2 (right axis). The ice particle grew in mass mainly by vapor deposition until it exceeded a radius of about 200 $\mu$m (at -21°C) at which the collection efficiency of cloud drops became appreciable. The riming growth rate increased rapidly as the size and terminal velocity of the particle increased coherently. At large particle size, toward the end of the fall trajectory, the total mass growth was due mostly to riming. It must be realized that the precipitation scavenging processes are decoupled from the background cloud and so the rime fractions represent upper limits. Curves A and B in Figure 4.2 represent the S(IV) scavenged by the total ice mass due to sorption ($C_L$) and entrapment ($L_B$), respectively. The removal of S(IV) at the upper part of the cloud was due entirely to sorption. The removal due to entrapment became significant at about -20°C due to the initiation of riming, and soon dominated the whole processes. Toward the end of the fall trajectory, the entrapment process accounted for about 87% of the total removal of S(IV).

The thick solid-line in Figure 4.2 represents the overall R.R.E. of S(IV). The magnitude of the overall R.R.E. is only 1% at the -30°C level due to a lower sorption effect at lower temperatures. The rather abrupt increase of the overall R.R.E. reflected the fact that the S(IV) concentration due to entrapment is still higher than that due to sorption, and that the rime fraction increases dramatically at about -20°C. The S(IV) R.R.E. by the ice particle reached a maximum value of about 6% at -15°C. It then started to show the decreasing trend with temperature of the entrapment factor and finally dropped to a value of 4% toward the end.
Figure 4.2: Cumulative S(IV) relative removal efficiencies (R.R.E., left axis) and rime fraction (right axis) of the ice particle at its cumulative size (top axis) and its falling position in the cloud (bottom axis). A: bulk sorption (from CL) in the depositional ice; and B: entrapment (from LB) in the rime ice. The thick-solid line (A+B) is the overall (sorption plus entrapment) relative removal efficiency in the ice particle. The thin-solid line shows the fraction of mass (right axis) of the ice particle that was grown by riming.
- Figure 4.3 compares the overall R.R.E. calculated from three different sorption parameterizations. Curve A is the surface sorption from CL; curve B, which is the same overall curve shown in Figure 4.2, is the bulk sorption from CL; and curve C is the bulk sorption from VDB. The individual R.R.E. due to entrapment, as shown by the dot-dashed-line (same as curve B in Figure 4.2), is also included for comparison. The sorption of S(IV) on ice in CL can be interpreted as a bulk (curve B) or a surface phenomenon (curve A). The bulk sorption (CL) has a stronger temperature dependence, which can be seen by comparing the coefficients $d$ and $d'$ in the exponential terms of (4.24) and (4.26), and also a higher value than the surface sorption as showed up in the figure. Note that the surface sorption phenomenon does not depend on the amount of depositional ice but on the surface area of the ice particle, which is due in part to the rime growth of the particle. Attention also has to be drawn to the fact that real ice particles often have larger surface areas than do the spheroid-shaped ice particles assumed in our model. Curve C shows a much larger R.R.E. due to sorption derived from VDB's parameterization, especially at lower temperatures. Since there is no temperature dependence in VDB's results, the extrapolation of their data to lower temperatures could be misleading. On the other hand, CL's experiment was done for ice particles in equilibrium with water vapor and might not represent the ice growth situation. Clearly, additional experimental work is needed to understand the sorption process for ice particles under realistic growth conditions at various temperatures. Also, the sorption and entrapment factors discussed above were measured in the SO$_2$ only environments. As shown by the difference between curves D and E in Figure 4.1, the presence of other trace gases will influence the pH and, hence, the removal efficiency of S(IV) in the aqueous-phase. Therefore, the addition of trace chemical species in the ice-phase system might also make a difference to the sorption as well as to the entrapment factors.
Figure 4.3: Overall cumulative S(IV) relative removal efficiencies (R.R.E.) of the ice particle due to entrapment in the rime ice plus three types of sorption in the depositional ice: A: surface sorption from CL; B: bulk sorption from CL; and C: bulk sorption from VDB. The portion contributed from the entrapment in the rime ice for curve A, B, and C is shown by the dot-dashed line (same as curve B in Figure 4.2). Top and bottom axes are the same as in Figure 4.2.
Extended work is also needed to study the sorption behavior of ice particles in the presence of more than one trace gas.

With the limited information available, the significance of ice-phase chemistry is demonstrated in our simple model. The removal of S(IV) in the ice-phase precipitation is quite different from that in the aqueous-phase. The microphysics also makes a great difference in the actual amount of S(IV) removal by different precipitation types.

The differential **R.R.E.** concept can be applied to the wet removal of chemicals in models that keep track of the condensate forms at each layer of the model atmosphere. The differential **R.R.E.** concept has direct implication to the calculation of the trace chemical concentration at different levels of the global background atmosphere. The cumulative **R.R.E.** concept can be used in models that consider only the net amount of precipitation at the surface.

### 4.1.6. Conclusion

The removal of trace chemicals from the atmosphere by precipitation can be parameterized by the combination of two types of parameters: 1) chemical parameters, and 2) microphysical parameters. The Henry's Law equilibrium concentrations of trace gases in the liquid are very useful chemical parameters which can be used in calculating the aqueous-phase removal processes. The ice-phase chemistry, which is typically neglected in most models, however, is potentially important because it exhibits complicated temperature dependencies and yields removal processes that cannot be completely ignored. Parameterization of the trace chemical concentration in the ice-phase can be related to the Henry's Law equilibrium concentration for each trace species in the liquid-phase by the entrapment factors and the sorption factors, which are
functions of temperature only. These two chemical parameters for S(IV) and some other trace species that have been studied experimentally are parameterized in this paper. Similarly, the ice-phase microphysical parameters associated with the entrapment and sorption factors can be related to the liquid-water or total condensed-water content by the rime-ice fraction and the depositional-ice fraction. These microphysical parameters, however, do not depend on temperature only, and need to be derived from a detailed microphysical cloud model.

A simple model following the above approach was developed to study the removal of trace chemicals by ice-phase precipitation, and to test different laboratory results of ice-phase chemistry. It was shown that the S(IV) removal efficiency by ice at each temperature level can be a significant fraction of water vapor removal. The concentration of S(IV) entrapped in the rime ice has a negative temperature dependence and is about one half to two orders of magnitudes smaller than that in liquid water. The S(IV) sorption onto the depositional ice has a positive or zero temperature dependence according to different laboratory findings. The [S(IV)] in the ice due to sorption can vary from near zero to two orders of magnitudes smaller than that in the liquid water. The overall S(IV) removal efficiency in the precipitation can be modified greatly by the types of growth processes. The sorption process is the primary mechanism for trace chemical removal at lower temperature levels where the ice grows primarily by vapor deposition. The entrapment process will become the dominant removal mechanism as the major growth process for the ice-phase precipitation switches to riming in the lower part of the mixed-phase cloud. The maximum S(IV) R.R.E. in ice-phase precipitation, using CL's sorption factor, is about 6% and occurs at about -15°C where riming starts to dominant the growth process and the entrapment factor is still greater than the sorption
factor. Using VDB's sorption factor, however, the maximum S(IV) R.R.E. occurs at low temperatures with a value of about 24%.

The concept of relative removal efficiencies, which relate directly to the chemical and microphysical parameters, is shown to be useful in the parameterization of the trace chemical wet removal. It can be applied, in a differential form, to atmospheric models with vertical resolution for the condensates or, in a cumulative form, to models that consider only the precipitation at the surface. With more laboratory study of the ice-phase chemistry and modeling study of the microphysics, the parameterization scheme for the wet removal of trace chemicals can be improved.
4.2. The Effect of Cloud Microphysics on the Composition of Rain


**Abstract.**

Cloudwater not only dissolves atmospheric aerosols and trace-gases but also provides an alternate medium in which chemical transformations may proceed at rates many orders of magnitude greater than similar gas-phase reactions. The composition of cloudwater, in turn, affects the rates and equilibria of the aqueous-phase chemical reactions and ultimately controls the spectral composition of rain. A detailed microphysical model is used to study the distribution of solute among the various condensate forms throughout a representative cloud. The emphasis of this work is to analyze the effect of various microphysical processes on the variation of solute concentration among drops of different sizes as well among drops within a given size category. It is found that, for drops formed in the same air parcel, the solute concentration varies with drop size due to differential nucleation and condensation growth paths that are related to the initial size distribution of condensation nuclei. For drops of similar size, however, variations of solute content arise primarily through hydrodynamic interactions between drops. The distribution of solute is further perplexed because drops of different origin and growth history may coexist in the same air parcel following differential sedimentation or by mixing processes. Such results provide valuable insights into the mechanisms of precipitation scavenging and a basis for interpreting field data.
4.2.1. Introduction

The chemical composition of cloudwater greatly influences the rates and equilibria of the aqueous-phase chemical reactions. Through aqueous-phase chemical reactions, atmospheric trace gases can be transformed into non-volatile forms that eventually contribute to the aerosol population. Through precipitation processes, some fraction of the atmospheric particles and some trace-gases can be scavenged and removed from the atmosphere. The portion remaining in the atmosphere can be drastically modified in both their size and spatial distributions and in their chemical compositions. These aerosol particles, in turn, serve as the condensation nuclei for subsequent cloud formation. It is through these non-linear and interactive microphysical and chemical processes that clouds help to regulate the global atmospheric cycles. Therefore, there is a need to better understand the microphysical and chemical processes that determine the composition of cloudwater and rain.

Clouds have frequently been the subject of modeling studies, especially with so-called bulk-water models. It has been recognized, however, that bulk-water parameterizations may give misleading results in cloud chemistry (Hegg, 1989; Hegg and Larson, 1990). Individual cloud droplets act differently from bulk water in many ways, especially since the size of a cloud droplet has a large effect on the rates of mass transfer of dissolved species in the aqueous phase. Due to their diverse growth pathways, drops of different sizes will have inherently different solute compositions and pH values, as shown in both observational and modeling works (Noone et al., 1988; Perdue and Beck, 1988; Ayers and Larson, 1990). In order to examine cloudwater composition and the associated chemistry more closely, it is necessary to employ more detailed treatments of drop microphysics.
Chemical equilibria and reaction rates in the cloudwater are controlled by the chemical composition and pH values (Millero et al., 1989; Jayne et al., 1990). As cloud drops grow through condensation of water vapor, their solute concentrations undergo dramatic changes. Therefore, in order to understand the aqueous-phase chemistry, it is necessary to pursue the microphysical aspects of how cloud drops grow. The first stage of the growth process, activation of cloud condensation nuclei (CCN), depends not only on the environmental parameters such as vapor density and updraft speed, but also on the property of the CCN themselves. An assumption typical in models containing simplified microphysics is the monodispersed CCN size distribution. Even most sophisticated models are usually constrained to at least assume that the CCN composition is uniform. Ayers and Larson (1990) used an externally mixed, two-component aerosol population as a source of CCN to investigate such assumption. Without allowing internal mixing within and between the two components, however, their model was restricted to the study of condensational growth only, no hydrodynamic interactions between drops were considered.

Hydrodynamic interactions are important for the formation of large precipitable cloud particles, with an inevitable mixing of all component properties of the cloudwater. The mass redistribution introduces a perturbation in the relationship between the drop size and solute content causing the cloud-drops to "forget" the original CCN size distributions. Therefore, drops of the same sizes do not necessarily have the same solute content, which may arise from hydrodynamic interactions or other processes such as turbulent mixing, sedimentation, and the melting of ice particles. The mixing of droplets of different pH and solute content yields solutions that are not in equilibrium with the atmosphere in which droplets originally equilibrated (Perdue and Beck, 1988). Mixing induced exchange of volatile gases between air and droplets not only complicates the modeling of chemical
equilibria and kinetics, but also limits the use of bulk samples for chemical analyses. Therefore, there is a clear need for a model that can give more detailed descriptions about the cloud particle sizes and properties. In this paper, we introduce a model that can deal simultaneously the detailed microphysics and chemistry and use it to describe the evolution of cloudwater composition from a microphysical point of view.

4.2.2. Numerical Methods

Within localized regions of a cloud, the atmosphere may be considered relatively uniform. Thus, it is convenient to subdivide the atmosphere into finite grid spaces and treat each portion as a homogeneous entity. Within that same region, however, it is often necessary to look at variations in some microscopic features of the cloud. In order to study an atmospheric aerosol system, such as a cloud, it is necessary to conceptually separate the particles from the gas-phase system and describe them according to their phases, abundances (i.e., number concentration), bulk properties (size, shape, density, surface area, etc.), and composition. Since it is impossible to keep track of particle properties on individual bases, numerical methods require the use of a few parameters in the modelling of atmospheric aerosol systems.

4.2.2.1. Bin Method

The bin (or "category") method approximates the aerosol system by grouping particles with similar properties into one bin. The main grouping parameter is the
number or number concentration. The sizes of the bins and the choice of categorization components are usually designed according to the specific applications and to the availability of computation resources. Bin methods are commonly used in the gridding of space in atmospheric dynamic applications and the drop-size categorization in cloud microphysics. Sophisticated microphysical models often use the bin method to obtain a detailed resolution of the cloud particle size spectrum. Since spatial gridding can be done in multiple dimensions, the categorization of particles is not limited to the size only. Shape factor, for instance, should be included as a categorical component to simulate cloud ice particles. In the study of cloudwater composition, the solute content should be considered as a bin component in addition to water mass (which generally determines the size).

During the growth or decay of particles, some mass (or any other extensive property) and some number of particles are frequently transferred between bins. The treatment of particle growth and inter-bin transfer is an essential issue in the bin method. Many early efforts have been made to solve the bin-transfer problem (Berry, 1967; Bleck, 1970; Egan and Mahoney 1972). However, some of them have either encountered numerical diffusion problems or failed to conserve the mass and number. Improved numerical methods, such as that proposed by Young (1974a), were developed using separate number and mass conservation equations, thus allowing for sub-bin resolution and accurate and efficient results. Such methods are conceptually similar to the "method-of-moment" (Tzivion et al., 1987), the "piecewise parabolic method" (Carpenter et. al., 1990) and the "particle-in-cell finite element method" (Bermejo, 1990).

The bin method used in this paper is an adaptation of the continuous sub-bin resolution concept with several improvements that make it more general and flexible. Although the traditional continuous-bin method can be used in the calculation of particle
growth, the combined growth equations are often not easy to solve. The alternative approach used here is to calculate a "mean" growth, thereby simplifying the growth equation and reducing the computational time without losing significant accuracy. A continuous-bin method is then used to calculate the particles transferred between bins. This method allows irregular (as opposed to linear or logarithmic) bin sizing factors and the transfer of particles over multiple bin-ranges, advantageous feature not possible in the "method-of-moments". Particle transfer in multiple-component space is also permitted to account for the simultaneous growth of more than one property of the drop.

4.2.2.2. Microphysics and Chemistry

The microphysics and chemistry of cloudwater are very complicated. Here, in order to simplify the discussion and concentrate on the microphysical aspects of the problem, the chemical equilibria and kinetic reactions are purposely neglected. Also, only one type of CCN solute content (ammonium sulfate) is treated in the model to show some basic effects of the microphysics on the redistribution of cloudwater composition.

The microphysical processes that are treated in detail are drop nucleation, diffusional growth, collision-coalescence, breakup and sedimentation. The calculation of the nucleation and diffusional growth of the cloud drops follows Köhler theory and Maxwell's two-stream growth theory (Pruppacher and Klett, 1980). Energy is preserved for each group of particles. Mass and energy balance between particles and the air are maintained through the mass and energy transfer equations. The stochastic collection equation is used for the hydrodynamic interactions (Pruppacher and Klett, 1980). The parameterization of collision efficiency is adapted from Lee (1990) with modifications to enable extrapolation to drop sizes greater than 140 µm in radius. The equation of
coalescence efficiency is from Low and List (1982a). The collision-breakup probability functions are tabulated using formulae in Low and List (1982b) with some adjustment for mass conservation. Sedimentation is calculated for drops in each bin according to their specific terminal velocity by applying the bin-method in the vertical grid component.

4.2.3. Model

4.2.3.1. Model Setup

Two bin-components, water mass and solute mass, are used to categorize the cloud particles. Forty bins were assigned to the water mass component, 15 bins to the solute content. The largest bin-limit has an equivalent radius of 4.5 mm over which drops are assumed to undergo aerodynamic breakup. The ratio of bin sizes (in mass) varies from 1.3 at the large end to 2.8 at the small end (Figure 4.4). Such arrangement gives better accuracy for the hydrodynamic interactions which are more important in the larger size ranges. The largest solute bin has a lower bin-limit equivalent to a dry ammonium-sulfate particle of 2 µm in radius and a free upper limit. The smallest bin has an upper bin-limit of 0.02 µm and a lower-limit near zero. The bin-sizing factor increases from 2 at the largest bin to 4.3 at the smallest. Note that the setting of near-zero lowest limit and free uppermost limit is not possible for logarithmically sized bins. Concentration isopleths are shown by the heavy lines.

A log-normal distribution is used for the initial ammonium-sulfate CCN. The appropriate water mass for each CCN is determined from their haze-state equilibria with the environment (Figure 4.4). The largest solute bin category (bin 15) has a mean
Figure 4.4. Initial setup of bins and particle distribution in water and solute components. Long and short horizontal axes are water and solute component bin numbers with subsidiary axes showing their equivalent number per mole of air. Heavy lines are the concentration isopleths.
equivalent dry radius of 2.3 µm and a wet radius of about 7.7 µm (bin 7) at 96% humidity. Note that although CCN in solute bin number 1 through 9 are all in water bin 1, they actually have different water masses that are within the first water-bin range. The total CCN number concentration is assumed to be 500 cm^{-3} at the surface and decrease exponentially with height. Vertical air motion, initiated after one hour of simulation time, is induced by a "mountain" with slopes that change according to a sine function and having a flat top at 3 km above ground level (Figure 4.5a). Updraft and downdraft speeds also change according the sine function with maxima of about 1.6 m s^{-1} (Figure 4.5b).

The first case simulates the condensational growth process. Figure 4.5c shows the changes of water vapor saturation ratio corresponding to the air motion. To contrast the microphysical effects, one additional process will be included in each subsequent case. Condensational growth, as well as the next two mechanisms considered, collision-coalescence and breakup, are simulated in a one-layer parcel model. To include the sedimentation effect, the fourth case is simulated in multiple layers.

4.2.3.2. Model Results

Haze particles, when in equilibrium with their environment, exhibit the highest solute concentration in those with the smallest size. However, there is a tendency for the smallest haze particles to catch up to the size of larger ones during condensational growth. Since the dilution effect is most prominent for the drops with the least initial solute content, the trend of solute concentration in the drops as a function of size is reversed from their original haze state with a large variation over a relatively short range.
Figure 4.5: Time profile of the model topography and related fields. (a) Height of mountain (1 hour is equivalent to a 36 km horizontal distance for a horizontal wind of 10 m s⁻¹). (b) Topography induced vertical air velocity. (c) Saturation ratio in the condensational growth case.
Figure 4.6 shows the evolution of drop sizes due to condensation. The ascending air becomes supersaturated at 1.1 hr and some of the haze particles start to nucleate. The first two solute bins (dry radius less than 0.02 µm) are not activated due to a limited supersaturation (about 0.3%) acquired in the ascending air. The remaining particles grow to a narrow size range of 20 to 40 µm in less than half an hour and remain in that size range until the air reaches the downdraft region. Note that the spreading of drops in a particular solute bin over two or three water bins is not an effect of numerical diffusion but a result of allowing partially occupied bins and the use of irregular bin sizing factors (which is smaller as drops grow larger).

Without other processes occurring simultaneously, the growth of droplets by vapor diffusion produces a fairly uniform and limited size distribution. Further broadening of the spectrum toward precipitable sizes is usually due to the collision-coalescence of drops. In the second simulation we turned on the coalescence process in addition to the condensational growth. The drop spectrum before 1.5 hr is not much different from that in the previous case. The coalescence process did not become important until some drops grew over 20 µm in radius, above which the collision efficiency becomes significant. Figure 4.7a shows that at 2 hr large drops start to form and the spectrum shifts toward higher bins in both components. The largest drops achieved are over 700 µm (bin 26) despite their negligible number concentration. However, more than one drop per mole of air reaching 200 µm in radius (bin 19) was produced. At 2.5 hr (Figure 4.7b) significant numbers of millimeter-size drops were generated with the largest radius reaching 3 mm. Note that solute bin 15 actually has a large dry size range and is a collect-all bin for all drops with dry solute size over 2 µm. The coalescence process broadened the drop spectrum in both water and solute
Figure 4.6: Evolution of drop spectrum due to condensation process: (a) 2.0 hr, and (b) 2.5 hr. Axes are the same as in Figure 4.4.

Figure 4.7: Same as Figure 4.6 but with additional coalescence process. Column with zero height indicates a value less than the lowest axis unit.
components and, therefore, perturbed the relationship between the drop size and the solute contents.

During the collision of two drops, some drop pairs will coalesce while others actually break up when the collision kinetic energy needs to be dissipated out through creating more surface area. As can be seen from Figure 4.8a, which is almost identical to Figure 4.7a, that breakup process is not prominent for drops with sizes less than a few tenths of a millimeter. Comparing Figure 4.8b with Figure 4.7b, we see that fewer drops have reached millimeter sizes at 2.5 hr than in the previous case. It is evident that breakup is the key process in limiting the growth of raindrops. Note that the air is motionless after 1.7 hr, with saturation ratios near but not exactly unity. Despite the fact that both the Kelvin effect and the Raoult effect are very small for these drops, a minimal supersaturation value must be maintained in between the equilibrium surface saturation ratio of the largest and the smallest drops. Therefore larger drops are constantly condensing while smaller drops are evaporating in the still air. Fragment drops that broke up from the large, diluted drops have large curvatures and low solute contents. They tend to evaporate faster than other drops. Such phenomena are manifested by the introduction of drops in the lowest solute bin with relatively small water masses in both Figures 4.8a and 4.8b.

The effect of sedimentation is studied by including several layers, which are drier and have less CCN, above the original air parcel. The 2.0 hr drop spectrum in the original (lowest) layer shows that there are fewer large drops due to precipitation (Figure 4.9a). However, more medium-sized drops appeared due to sedimentation from upper layers. At 2.5 hr, both the large and medium-sized drops decrease in number while drops of less than 30 µm in radius remain at about the same number concentration (Figure 4.9b).
Figure 4.8: Same as Figure 4.7 but with additional breakup process.

Figure 4.9: Same as Figure 4.8 but with additional sedimentation process.
4.2.4. Discussions

The history of drop growth can be separated into several phases. The nucleation and condensation processes control the early stage of drop size and solute evolution. The coalescence process starts to occur after drops larger than 20 µm in radius appear. The onset of breakup follows when drops of at least a few hundred micrometers in radius appear. Sedimentation preferentially filters out larger drops and mixes up particles from different origins. Figure 4.10 shows the drop size evolution by summing up the number of drops over the entire solute range for each water bin. Condensation tends to produce a narrow drop size distribution (Figure 4.10a). The result of coalescence is to broaden the drop spectrum and produce a second mode in the mass distribution function (Figure 4.10b). The breakup process tends to offset the effect of coalescence and slow down the drop size evolution (Figure 4.10c). Sedimentation produces a downward flux of number concentration. Its net effect depends on the vertical profile of air properties. In the present case, there is a net loss of larger drops and a temporary gain of hundred micrometer radius drops at the 2 hr simulation time (Figure 4.10d).

Microphysical processes not only drive the evolution of drop sizes but also the evolution of the solute spectrum as shown in Figure 4.11. Condensation has no effect on the solute distribution (Figure 4.11a). Coalescence process forces drops to combine both water and solute masses. Figure 4.11b shows that the solute distribution shifts toward the largest solute bin when there is significant coalescence. Breakup, on the other hand, tends to restore the original CCN distribution (Figure 4.11c). Sedimentation is a removal process that is most significant for large drops. Figure 4.11d shows that large drops that come with the most solute content precipitate out most effectively from the air. Since the non-precipitating drops will eventually evaporate and return to the CCN population, the microphysical processes have definite influence on the CCN distribution.
Figure 4.10: Drop mass distribution in water component for (a) condensation; (b) coalescence; (c) breakup; and (d) sedimentation cases. Long horizontal axis is the water bin number, short axis is the simulation time at 1.0, 1.5, 2.0 and 2.5 hr. Vertical axis is $10^6$ times mole of water per mole of air in log-scale.
Figure 4.11: Same as Figure 4.10 except for the distribution in the solute component. Vertical axis is $10^{-13}$ times mole of ammonium-sulfate per mole of air in log-scale.
4.2.5. Conclusions

The variation of cloudwater and precipitation composition is strongly dependent on the cloud microphysical processes. For drops formed in the same air parcel, the solute concentration varies with drop size due to differential nucleation and condensation growth paths that are related to the initial size distribution of condensation nuclei. Without other microphysical processes, solute concentration in cloud drops can vary drastically within a narrow range of sizes. Hydrodynamic interactions, however, tend to disturb the one-to-one relationship between cloud drop size and solute concentration. The distribution of solute can be further perplexed by mixing drops of different origin and growth history through sedimentation process. Processes that are not included in this study, such as nucleation of CCN with mixed-composition, ice-liquid phase transitions, turbulent mixing and chemical reactions, may have even more complicated effects on the cloudwater composition. All these processes can not only complicate the simulation of cloud chemistry and precipitation scavenging, but they also cause difficulties with interpreting on precipitation sampling. Detailed microphysical and chemical models, as introduced here, can help to achieve a better understanding of cloud and precipitation scavenging.

Note: The discussions on this paper occurred in the Fifth International Conference on Precipitation Scavenging and Atmosphere-Surface Exchange Processes (Richland, WA, July 15-19, 1991) are listed in Appendix B.
4.3. The Evolution of Saturation Ratio

The material in this section is adapted from a paper published in the *Preprints*, Eleventh International Conference on Clouds and Precipitation, Montreal, Canada, August 17-21, 1992, pp. 322-325.

4.3.1. Introduction

Saturation ratio represents the amount of water in the gas-phase that constantly interacts with the condensed-phase particles in the cloud. It not only reflects the details of ongoing microphysical processes but also governs the nucleation and subsequent growth of both cloud droplets and ice particles, and ultimately determines the formation of precipitation. Simple cloud models that cannot properly resolve the change of the saturation ratio will not be able to accurately simulate the cloud processes, especially when ice-phase microphysics are involved. For instance, rapid glaciation with ice number concentrations of over several hundreds per liter has been frequently observed to exist in the tops of cumuliform cloud (Coons and Gunn, 1951; Koenig, 1963; Hallett et al., 1978; and Hobbs and Rangno, 1990). Rangno and Hobbs (1991) suggested that such phenomena could be result from the enhanced ice-nucleation activity at very high water saturations. Thus, any factor that controls the saturation ratio may have a strong influence on the ice nucleation process. Extensive studies have demonstrated the effect of updraft speeds and CCN distribution on the development of supersaturation (e.g., Howell, 1949; Squires, 1952; Lee et al., 1980). Some attention has also been paid to the effect of the liquid-phase hydrodynamic interactions (e.g., Young, 1974c; Ochs, 1978). Little work, however, has been done in examining other factors that are strongly related to the development of saturation ratio. In this paper we use a detailed microphysical cloud
model to study the evolution of the saturation ratio and the factors that control it. Several scenarios are designed to investigate the sensitivity of the saturation ratio to each of the controlling factors. Some emphasis will also be placed on the effect of the liquid-phase microphysics on the formation of ice particles through the development of supersaturation.

4.3.2. Theory

The two basic factors that control the saturation ratio in an air parcel are: (1) the intensity of the upward motion that causes the adiabatic cooling of air and acts as the source of excess water vapor; and (2) the available surface area of cloud particles that water vapor may deposit onto. Squires (1952) derived the supersaturation development equation:

\[
\frac{ds}{dt} = A_1 W - A_2 \frac{dm}{dt}
\]

Here, \( s \) is the supersaturation ratio, \( W \) the updraft velocity, \( A_1 \) and \( A_2 \) are functions of air properties (temperature and pressure), and \( \frac{dm}{dt} \) the overall rate of vapor deposition onto cloud particles. In liquid-phase clouds, the deposition rate is controlled by the initial cloud condensation nuclei (CCN) distribution and the microphysical processes that affect the drop size distribution and hence the total surface area. We can thus categorize the controlling factors of the supersaturation development into: (1) microphysics, (2) updraft velocity, (3) CCN distribution, and (4) air properties, which will be examined separately in the first part of our model simulation.

The presence of ice particles in the mixed-phase clouds can provide more surface area for a more effective rate of vapor deposition than cloud drops do. On the other
hand, it also reduces the total surface area through the hydrodynamic collection of droplets. To study ice-phase processes, it is essential to know the mechanisms of ice generation. Among the various modes of ice nucleation, the heterogeneous deposition-nucleation is usually the most effective in the updraft region of clouds. In his experimental studies, Fletcher (1962, pp 241-242) measured the ice number concentration as a function of temperature in a water-saturated environment and gave the empirical relationship:

$$N = N_o \exp(\beta \Delta T), \quad (4.28)$$

where $N$ is the number concentration of ice nuclei active at a supercooling of $\Delta T$, $N_o$ and $\beta$ are constant. However, Huffman (1973) suggested that this temperature dependence is merely reflecting the temperature dependence of the ice saturation ratio at 100% liquid water-saturated environment. The number concentration of ice particles actually depends on the supersaturation over ice according to the power-law relationship:

$$N = c s_i^\alpha, \quad (4.29)$$

where $c$ and $\alpha$ are constants, and $s_i$ is the supersaturation over ice. The second part of our model simulation will emphasize the effect of ice-phase microphysics on the saturation ratio, as well as the effect of saturation ratio on the ice nucleation according to the power-law relationship (4.29).

### 4.3.3. Model Description

To properly simulate the physical and chemical changes of cloud particles, a multi-component particle framework is developed which categorizes cloud particles into different bins according to several major properties of the particles. The liquid-phase
particle framework is two-dimensional with 45 bins in the water-mass component and 20 bins in the solute-mass component. An extra component, the aspect ratio, with 10 bins is applied to the ice-phase particle framework. The transfer of particles between bins for the growth in various bin-components is calculated with a "method of moments" type scheme that conserves both the number and the component value. Other particle properties, such as temperature and ice particle density, are preserved without the detailed categorization treatment.

In the present study, ammonium-sulfate is used as the solute component. An initially log-normal distribution (dry size) is assumed for the sulfate particles, which act as cloud condensation nuclei. Liquid-phase microphysics considered are the nucleation, condensation, and stochastic collision-coalescence/breakup of droplets. Detailed ice-phase microphysics are also included with the shapes of ice particles approximated by oblate and prolate spheroids. Ice nucleation mechanisms included are the heterogeneous deposition-nucleation, the homogeneous and heterogeneous freezing, the contact freezing, as well as the secondary ice generation by rime-splintering. Diffusional growth of ice particles is computed using the electrostatic analogy for both mass and heat transfer. The treatment of the linear growth rates on the prism and basal faces is based on both theoretical and experimental results, but the details will not be addressed here. The growth of ice particles by accreting droplets is calculated with the stochastic approach with collision efficiencies based on experimental studies.

4.3.4. Simulations and Discussions

To analyze the various factors that determine the saturation ratio, a parcel model with constant updraft speed is used to simplify the basic physics. The first four
sensitivity tests on the evolution of the saturation ratio in warm clouds will be done by varying the following parameters: (1) liquid-phase microphysics, (2) updraft speed, (3) CCN number concentration ($N_{CCN}$), and (4) air properties. For the purpose of comparison, a standard scenario will be appearing throughout each sensitivity study with $W = 2 \, \text{m s}^{-1}$; $N_{CCN} = 500 \, \text{cm}^{-3}$, and cloud base at $T = 5 \, \text{oC}$ and $P = 990 \, \text{mb}$. One parameter will be allowed to vary in each case. The role of ice-phase microphysics will be demonstrated in the fifth case. By varying the CCN concentration and checking its effect on the number concentration of ice particles, we will also show the inter-connections between the liquid- and ice-phase processes through the saturation ratio.

**Case a: Liquid-phase microphysical factors.**

Before the activation of CCN in an ascending air parcel, the saturation ratio increases monotonically as the saturation vapor pressure is depressed upon the cooling of air by expansion. At this stage, the source term in (1) dominates the change of $s$. Once saturation is reached, large CCN particles activate and form cloud drops, which then continuously provide more surface area for further water vapor deposition. Thus, during the early nucleation stage, more and more CCN are nucleated as the saturation ratio builds up. The sink term in (1) increases rapidly while the source term remains fairly constant. As indicated by the point $A$ in Figure 4.12, the saturation ratio reaches a maximum once the effect of increasing surface area surpasses that of expansion cooling. When the saturation ratio starts to decrease, the activation of more CCN ceases to occur so that the total number of cloud droplets stays fairly constant. After point $A$, the depositional growth of drops increases the total surface area while depressing the saturation ratio. The net effect is that the sink term in (1) gradually reduces to a value approaching that of the source term. Without other microphysical processes involved,
the saturation ratio will tend to reach an equilibrium value as shown by the curve \(a\) in Figure 4.12. However, as cloud drops reach certain sizes (the Hocking limit), coalescence starts to occur as droplets collide with each other due to differential fall velocity. Curve \(b\) shows the evolution of the saturation ratio when the collision-coalescence process is included. The saturation ratio starts to rise at point \(B\) when the droplets grow large enough by deposition to coalesce. This is due to the decrease of total surface area as droplets coalesce with each other. Since the ability of collecting smaller drops increases as droplets grow larger, the effect of coalescence is cumulative once it is started. This can be seen from the exponential increase of the saturation ratio. Curve \(c\) shows the evolution of the saturation ratio when the collision-breakup process is allowed. The breakup process tends to offset the effect of coalescence, but it will not occur until the colliding drops exceed several hundred \(\mu\text{m}\) in size. Thus, the effect of breakup on the saturation
ratio will not be significant until a later time. The results up to this point are similar to those in Young (1974) and Ochs (1978). Note that the temperature curve in Figure 4.12 can be applied to all events except those in Case b with updraft velocities other than 2 m s\(^{-1}\) and those in Case d with different cloud-base temperatures. Also, curve c in the first four figures is the same curve from the standard run.

**Case b: Effect of updraft velocity**

Upward motion in the atmosphere causes the air to cool by expansion. The cooling of air directly leads to the increase of the saturation ratio as shown in equation (1). Thus, a stronger updraft means a stronger source term in the *supersaturation development equation*. Consequently, the balancing point between the source and sink

![Figure 4.13: Evolution of saturation ratio with updraft speed of (a) 0.5 m s\(^{-1}\), (b) 1 m s\(^{-1}\), (c) 2 m s\(^{-1}\), and (d) 4 m s\(^{-1}\).](image)
terms will be greater with stronger updraft. This is reflected by the higher maximum saturation ratio for larger $W$ in Figure 4.13 (note the change in scale). Also, the saturation ratio is higher throughout the time so that the droplets always grow faster in stronger updrafts. The deposition growth rate is very important in determining the timing of the onset of the hydrodynamic interactions. As shown in Figure 4.13, the hydrodynamic interactions start earlier with $W = 4 \text{ m s}^{-1}$ (curve d) than the standard run with $W = 2 \text{ m s}^{-1}$ (curve c). When the updraft speed is small, the coalescence process might not start in time (curve a, b). Note that the kink in curve d, as indicated by the point A, results from the re-enabled nucleation of the previously inactivated CCN as the saturation ratio exceeds the initial maximum. The newly activated drops produce more surface area that reduces the rate increase of the saturation ratio.

**Case c: Effect of CCN number concentration**

The magnitude of the sink term in (1) is directly related to the CCN number concentration during the nucleation stage. Higher $N_{\text{CCN}}$ means more drops will be nucleated at the same updraft speed and supersaturation. As shown in Figure 4.14, the maximum saturation ratio increases with lowered $N_{\text{CCN}}$. With fewer cloud drops formed, the equilibrium saturation ratio is higher when other parameters are kept the same. Therefore, those fewer droplets grow faster due to the higher supersaturation. Similar to the previous case, faster deposition growth will initiate the hydrodynamic interactions earlier. With only 20 cm$^{-3} N_{\text{CCN}}$, the hydrodynamic interactions start about 10 min earlier than the one with 100 cm$^{-3}$ (curve b), and 20 min earlier than the standard case (curve c). For $N_{\text{CCN}}$ of 2500 cm$^{-3}$, the droplets do not grow large enough to initiate the hydrodynamic interactions until a much later time. The re-enabled nucleation also shows up at point A of curve b. However, such a kink in the curve does not occur further
Figure 4.14: Evolution of saturation ratio with varying CCN number concentration of (a) 20 cm$^{-3}$, (b) 100 cm$^{-3}$, (c) 500 cm$^{-3}$, and (d) 2500 cm$^{-3}$.

down the curve, and does not show up in curve a at all due to the availability of residue CCN. With very few CCN left, not much new surface area could be created to have any significant effect on the existing trend.

**Case d: Effect of air properties**

The effect of air properties shows up in the coefficients $A_1$ and $A_2$ in (4.27). Figure 4.15 (with vertical scale the same as Figure 4.12) shows the evolution of saturation ratio in air parcels with cloud-base temperatures of 25 °C (curve a), 15 °C (curve b), 5 °C (curve c), and -5 °C (curve d). Clouds formed at higher temperatures will have lower saturation ratio maxima. This means fewer CCN are activated in warmer clouds. The saturation ratios for colder clouds are generally higher. However,
this higher saturation ratio does not readily translate into a faster growth rate since the
deposition growth rate also depends on temperature. In fact, the growth rate is directly
proportional to the vapor density difference between drop surface and air, which tends to
be larger at higher temperature according to the Clausius-Clapeyron equation.
Therefore, the hydrodynamic interactions start sooner in warmer clouds as shown by the
earlier increase of saturation ratio in curves of higher cloud-base temperatures. The
re-enabled nucleation (point A and B) is even more distinct in this case than in the
previous cases because more interstitial CCN are available.

Figure 4.15: Evolution of saturation ratio with various cloud-base temperatures of 25 °C
(curve a), 15 °C (curve b), 5 °C (curve c), and -5 °C (curve d). The four arrows to the left point
to the saturation maxima of each curve.
**Case e: Ice-phase microphysical factors.**

Ice particles are more efficient in growing by either vapor deposition or hydrodynamic interactions than droplets. The liquid-phase effects on the evolution of saturation ratio discussed previously will be even stronger for ice-phase processes. Figure 4.16 shows the saturation ratio profile for only depositional growth of droplets and ice particles (curve \(a\)), adding the liquid-phase hydrodynamic interactions (curve \(b\)), and with the additional riming process (curve \(c\)). With only depositional growth, as shown in curve \(a\) of the upper graph, the saturation ratio evolves in a similar way to the 'condensation only' scenario in **Case a**, except for a lower saturation ratio toward the end (not obvious in the graph owing to the small scale). These lowered saturation ratios result in a slower condensational growth of droplets so that the initiation of liquid-phase hydrodynamics is delayed, as can be seen from curve \(b\). The bottom graph of Figure 4.16 demonstrates the number concentrations of ice particles corresponding to the upper graph. The number concentration of ice particles follows the power-law dependence on the ice supersaturation in equation (3). The freezing-nucleation modes are insignificant here partly due to the depletion of droplets by riming. The number concentrations in scenarios \(a\) and \(b\) are just slightly more than what can be provided by the "basic" ice-supersaturation corresponding to the 100% water saturation. It reaches about 200 mol\(^{-1}\) (about 6 per liter) at -20\(^\circ\)C. The hydrodynamic interactions start too late to give significant enhancement in the ice nucleation. The riming process, however, is very effective in reducing the total surface area and enhancing the supersaturation, as shown by the curve \(c\) in the upper graph. The few ice particles that nucleated under the "basic" supersaturation can grow to a size that is effective in accreting droplets in a very short time through the *Bergeron-Findeisen process*. The saturation ratio, at first, increases as the ice particles deplete cloud drops. The increase in the saturation ratio, in turn, helps to
Figure 4.16: Evolution of saturation ratio (top) and the number concentration of ice particles (bottom) for (a) liquid- and ice-phase deposition growth, (b) additional liquid-phase hydrodynamic interactions, and (c) additional riming.
nucleate even more ice particles. This multiplying process is eventually self-terminated
due to the overwhelming production of new surface area of ice particles. The saturation
ratio then decreases and approaches the 100% ice saturation ratio. Again, notice the
re-enabled CCN nucleation at point A. Curve c in the bottom graph shows that the
number concentration of ice particles stops to increase when the saturation ratio reaches a
second maximum, a situation similar to that of the drop number concentration after the
first saturation ratio maximum. The number concentration of ice particles is more than
doubled when riming is included.

**Case f: Effect of CCN on ice nucleation.**

The previous case demonstrated that ice nucleation will occur naturally in the cold
regions of supercooled clouds as the ice supersaturation increases with decreasing
temperature in a water-saturated environment. However, it is possible to initiate ice
nucleation at higher temperatures by enhancing the saturation ratio through the
controlling factors mentioned earlier. Here, we use CCN number concentration as an
example to demonstrate this effect. Figure 4.17 gives the evolution of the saturation
ratio with various \( N_{CCN} \) and full microphysics. Note that curves c's are the same as those
in Figure 4.16. We can see that air with lower \( N_{CCN} \) can initiate ice nucleation earlier
and obtain higher number concentrations of ice particles. However, for \( N_{CCN} \) near or
above 500 cm\(^{-3}\), there is not much difference in the ice nucleation due to the limited
enhancement of supersaturation. The efficiency of ice accreting droplets is apparently
similar for those with high \( N_{CCN} \). By comparing curves c and d, one may find that the
one with higher \( N_{CCN} \) is even slightly more efficient in riming than that with lower \( N_{CCN} \).
This might result from the larger fall-speed difference between the collector ice and the
droplets that are smaller with respect to the higher \( N_{CCN} \).
Figure 4.17: Evolution of saturation ratio (top) and the number concentration of ice particles (bottom) with full microphysics and various CCN number concentrations.
4.3.5. Conclusions

Although neither entrainment nor sedimentation is considered, an air parcel model with detailed microphysics provides a systematic examination of the evolution of saturation ratio and the factors that control it. Cloud drops need to grow by vapor deposition to a certain size before they are capable of growing by coalescence and forming precipitation. The development of supersaturation is very important to the timing of this growth-mode transition from vapor deposition to hydrodynamic collection. Updraft speed, CCN number concentration, cloud-base temperature and other parameters that can influence the saturation ratio in clouds are all controlling factors of precipitation formation. From the evolution of the saturation ratio, the signatures of the ongoing microphysics are reviewed. Saturation ratio is also crucial to the ice nucleation. The enhancement of supersaturation through various microphysical processes may be partly responsible for the observed high number concentrations of ice particles in the relatively warm region of mixed-phase clouds.
4.4. The Simulation of a Two-Dimensional Steady-State Orographic Cloud

With the full microphysics and chemistry described in previous chapters, the model is applied to simulate a two-dimensional steady state orographic cloud. This simulation uses a case provided in the Third International Cloud Modeling Workshop held in Toronto, Canada, August 10-14, 1992. The data were obtained during the Sierra Cooperative Pilot Project (SCPP), a cloud seeding investigation conducted in the Sierra Nevada Mountains of California.

4.4.1. Model Setup

Particle frameworks

The two bin-components used for the liquid-phase particle framework are the mass of water and the mass of sulfate. There are 45 bins for the water component. The largest bin has a upper limit of \( m_46 = 0.0212 \) mol, corresponding to a radius of 4.5 mm. The lower bin-limits of successive smaller bin are defined as

\[
m_i = m_{i+1} / q_{i+1},
\]

where \( q \) is the bin-sizing factor, which itself is modified by a constant \( \theta \) so that \( q_i = \theta q_{i+1} \).

We thus have

\[
m_i = m_{i+1} / q_{i+1} = m_{i+2} / q_{i+1} = \ldots = m_n / q_{n+i} = \frac{m_n}{q_i \theta^k},
\]

where \( k = \frac{(n-i)(n-i)}{2} \). By letting \( \theta > 1 \), we give higher resolution to the bins at the larger end of the spectrum, whereas by letting \( \theta < 1 \) we give higher resolution to the smaller end of the spectrum. When \( \theta = 1 \), the scheme reduces to the commonly used
logarithmic sizing oh the bins. As discussed in Section 3.1, it is desirable to have a finer resolution at larger size ranges, where the coalescence process is important. The values of $q_{46} = 1.3$ and $\theta = 1.02$ are thus used here. The upper limit of bin 1 (or the lower limit of bin 2) $m_2$ is then $4.58 \times 10^{-15}$ mol (equivalent to 0.27 $\mu$m in radius). The lowest mass limit $m_1$ is relaxed to $2.3 \times 10^{-22}$ mol (equivalent to about 140 molecules), which should be enough to cover the smallest possible value.

There are 20 bins used for the sulfate component. The largest bin has an upper limit of $m_{21} = 1.47 \times 10^{-8}$ mol, corresponding to a dry ammonia sulfate particle of 64 $\mu$m in radius, which should be enough to cover the largest possible value in nature. The lower limit of the largest bin is $m_{20} = 4.486 \times 10^{-13}$ mol, which is equivalent to a dry radius of 2 $\mu$m. The bin sizing factors for the sulfate component are $q_{21} = 2.0$ and $\theta = 1.025$. Therefore, the upper bound of bin 1 is $m_2 = 1.19 \times 10^{-19}$ mol (0.13 $\mu$m). The lowest bin limit is set to be $1.0 \times 10^{-22}$ mol.

For ice-phase particle frameworks, the water and sulfate components are the same as that for the liquid-phase framework. Another variable, log $\phi$ (log aspect ratio), is used as the third component with 11 bins. The lower limit of the largest bin is set to be 1.3 ($\phi \approx 20$) and the upper limit of the smallest bin is -1.3 ($\phi \approx 1/20$). The bin limits in between are then linearly interpolated. The smallest and largest bin limits are set to extreme values of -5 and 5, respectively.
Initial conditions

The CCN spectrum is assumed to be log-normally distributed (same as that used in Section 4.2) with mode at 0.05 µm in radius and standard deviation of 0.9. The total number concentration $N_{CCN}$ is assumed to be 500 cm$^{-3}$ near the ground, and decreases exponentially upward according to a formula that was obtained by reading from Figure 8-10 in Pruppacher and Klett (1980, p. 208):

$$N_{CCN}(z) = N_{CCN}(0) \exp(-2.8 \times 10^{-4} \text{ m}^{-1} z) .$$  \hspace{1cm} (4.32)

The total potential IN number concentration is assumed to be 230 l$^{-1}$ throughout the domain. The trace gas mixing ratios are 350 ppm for CO$_2$, 0.5 ppb for NH$_3$, 10 ppb for SO$_2$, 1 ppb for H$_2$O$_2$, and 20 ppb for O$_3$, all assumed to be constant throughout the vertical domain. Note that these values are only hypothetical since no measurements of these variables were made in the field study. The vertical profiles of temperature, pressure, and humidity are obtained from the Sheridan sounding at 18 GMT, December 18, 1986, as shown in Figure 4.18.
Figure 4.18: Sheridan sounding at 18 GMT, December 18, 1986. Thin horizontal lines are air pressures (mb), thin diagonal lines are air temperatures (°C), dashed lines are the dry-adiabats (°C), and thin-dotted lines are the saturation adiabats (°C). The thick curves denote the profiles of temperature (right) and dew-point (left).
Wind fields and spatial framework

In this simulation, 13 vertical layers in the vertical are applied. Each layer is initially 300 m in thickness. The bottom layer has initial lower and upper boundaries of 200 m and 500 m above the mean sea level (MSL), respectively. The top layer then has an initial upper boundary of 4100 m MSL. Cloud particles that fall below the lower boundary of the bottom layer are considered to be intercepted by the ground and counted as precipitation. Note that slight distortions in later graphic presentations tend to occur near the top and bottom of the model domain, where there are no actual data points outside those 13 layers.

The wind fields were calculated with the GUIDE diagnostic model (c.f., Rauber et al., 1988) and provided to the participants of the Third International Cloud Modeling Workshop; these are used for the prescribed winds needed for this simulation. The vertical and horizontal wind speeds were first constructed into lookup tables. The flow speeds at certain location are obtained by a cubic spline interpolation from the lookup tables. Each layer of a parcel, as well as its upper and lower boundaries, then follows the air-flow over the Sierra Nevada Mountains. Therefore, this simulation applies a parcel model within an Eulerian spatial framework.

Figure 4.19 shows the air flow trajectories and the smoothed topography. The air follows trajectories that are basically parallel to the terrain for the first 60 km in the horizontal model domain (HMD). Then, the effect of gravity waves causes the air above the 3.5-km level to move downward, while the air below still moves upward until it reaches the Sierra Nevada Crest. A similar phenomenon also occurs during the upslope of the Carson Range. The magnitude of the vertical motion above the Lake Tahoe Valley is quite a bit larger than that during the upslope of the Sierra Nevada.
Since the horizontal wind speed is not constant with height, each layer will take different amount of time to reach a certain horizontal location. Therefore, the constant time step commonly used in parcel models cannot be applied here, so a constant horizontal-distance step of 25 m was used instead. The time step is then determined from the horizontal wind speed divided by the fixed horizontal distance for each layer. Such an arrangement gives a two-dimensional steady-state simulation. Note that the microphysics is assumed to be not interactive with the dynamics (i.e., the microphysics does not alter the air flow). Also, mixing or entrainment is not included. Such assumptions are adequate for such wintertime orographic clouds.

Figure 4.19: Air flow trajectories over the Sierra Nevada Mountains. The shaded area represents the smoothed topography.
4.4.2. General Cloud Features and Microphysical Properties

The general features and the microphysical properties of the simulated cloud are summarized in the following five parts: (1) the air properties, (2) the liquid-phase properties, (3) the ice-phase properties, and (4) the aerosol particle concentrations, and (5) the precipitation.

Air properties

Figures 4.20 and 4.21 show the temperature and humidity profiles of the simulation. The temperature fields are quite stratified. Following one of the trajectories, one therefore finds that cooling occurs during ascending motions and warming occurs during descending motions (Figure 4.20). As the air cools during ascent, the humidity of the air increases until it reaches water or ice saturation, at which point the cloud particles can grow. The shaded area on Figure 4.21 indicates the region where a saturation ratio with respect to water $S_w$ exceeds unity (100% relative humidity) and where the liquid cloud can be formed. Note that ice particles may form either inside or outside this region, depending on the air temperatures and whether the saturation ratio with respect to ice $S_i$ is reached. The areas with $S_w > 1$ are within the two regions of upward motion and disappear when the air is descending. There are generally two cloudy areas that formed at (1) the upslope regions before the Sierra Crest, which is at about 100 km in the horizontal model domain (HMD), and (2) the upslope of the Carson Range, which has its crest at about 140 km HMD. We shall refer to the first cloud as the Sierra cloud and the second as the Carson cloud in later discussions.
Figure 4.20: Temperature profiles of the orographic cloud simulation. Contour interval is 2°C.

Figure 4.21: Saturation ratio profiles of the orographic cloud simulation. Contour interval is 0.05 (5% humidity).
**Liquid-phase fields**

Although the drop spectra are resolved in detail in this model, we can subdivide the whole spectrum into several bulk categories for simplicity of the discussion. For the liquid-phase particles, we define (1) aerosol particles (haze drops) with radius $r_d < 5 \, \mu m$; (2) cloud drops with $5 \, \mu m \leq r_d \leq 50 \, \mu m$; and (3) drizzle/rain drops, with $r_d > 50 \, \mu m$.

The water mass contained in the aerosol particles is normally insignificant. However, the number concentration of the aerosol particles is an important microphysical parameter, which will be discussed later.

Figure 4.22 shows the distribution of water mass content due to the cloud drops. The Sierra cloud has a larger cloudy area and maximum cloud water content in excess of $0.7 \, g \, m^{-3}$, located at about 64 km HMD and about 3 km MSL. The cloud is in contact with the ground at about 60 km HMD and dissipates on the lee side of the Sierra Nevada Crest. The Carson cloud is smaller than the Sierra cloud due to the short upslope distance. It has maximum liquid water content in excess of $0.8 \, g \, m^{-3}$ at about 130 km HMD and 3.6 km MSL. The Sierra cloud is about 3 km in depth, with tops of the liquid zone near the -15 °C level. The Carson cloud is about 2 km deep and the liquid zone also reaches the -15 °C level. The two clouds are mostly in the sub-freezing temperature regions, except the lowest part of the Sierra cloud at between 65 and 70 km HMD and below 1.5 km MSL.

Figure 4.23 shows the cloud drop number concentrations. The Sierra cloud has a maximum drop number concentration of over 80 cm$^{-3}$ (at 25 km HMD and 3.5 km MSL), while the Carson cloud has a maximum drop number concentration of just over 120 cm$^{-3}$ (at 128 km HMD and 2.7 km MSL). The maximum drop number concentration in the Carson cloud is higher than that in the Sierra cloud, mainly due to the stronger updraft along the steeper upslope zone of the Carson Range.
Figure 4.22: Cloud drop mass content in the simulated orographic cloud. Contour interval is 0.05 g m$^{-3}$.

Figure 4.23: Cloud drop number concentration in the simulated orographic cloud. Contour interval is 10 cm$^{-3}$.
The number concentration of cloud drops is determined by the updraft speed at the very beginning of cloud formation, unless the increase of the updraft speed is quite large. Therefore, there is no increase in the drop number concentration even though the slope and the updraft near the Sierra Crest are quite large.

The mass content of drizzle/rain is shown in Figure 4.24. In the Sierra Cloud, the drizzle/rain does not appear before 60 km HMD, which indicates that the cloud drops are still too small to have significant coalescence to form larger drops. As time goes on, the liquid water content increases with the degree of uplift and expansion cooling, and some fortunate drops can reach significant sizes to form drizzle after about 60 km HMD. The formation of drizzle is also indicated by the regions where the cloud water content (Figure 4.22) and the cloud number concentrations (Figure 4.23) are decreasing significantly. The maximum drizzle/rain mass contents in the Sierra cloud are about 0.3 g m\(^{-3}\) and located near the ground at 82 km HMD and 100 km HMD. A third maximum exists at a level of 1 km above the ground (2.5 km MSL) at 75 km HMD. The relative low altitude of the drizzle/rain fields is an indication of sedimentation. The drizzle/rain content in the Carson cloud has a maximum of over 0.2 g m\(^{-3}\) near the ground at 145 km HMD. Note that now drizzle/rain are formed within a shorter period of time. This could be a result of the large CCN formed from the evaporation of large drops in the previous cloud formation. These large CCN grow preferentially by condensation and can reach the sizes for significant coalescence in a rather short time. Alternatively, there might be some drops that remained from the Sierra cloud and had not fully evaporated into haze drops in the subsaturated downdraft above the Lake Tahoe Valley. The number concentration of drizzle/rain has a maximum of 100 per liter in the Sierra cloud and 70 per liter in the Carson cloud, as shown in Figure 4.25.
Figure 4.24: Drizzle/rain mass content in the simulated orographic cloud. Contour interval is 0.05 g m$^{-3}$.

Figure 4.25: Drizzle/rain drop number concentration in the simulated orographic cloud. Contour interval is 10 per liter.
**Ice-phase fields**

The ice particles are grouped into four bulk categories: 1) small cloud ice, with melted-equivalent radius $r_i < 5 \, \mu m$; 2) planar ice, with $r_i \geq 5 \, \mu m$ and aspect ratio $\phi < 1$; 3) columnar ice, with $r_i \geq 5 \, \mu m$ and $\phi > 1$; 4) graupel, once $r_i \geq 50 \, \mu m$ and $0.2 < \phi < 5$.

The criterion for graupel is based on the fact that large ice particles grown purely from water vapor normally are usually very elongated (columnar ice) or flat (planar ice). Ice particles with $r_i > 50 \, \mu m$ and aspect ratio between 0.2 and 5 are normally very heavily rimed, and can be considered as graupel. Note that the criterion for graupel takes precedence over that for planar and columnar ice particles. The growth of ice particles by vapor diffusion immediately after their nucleation is normally very rapid. Therefore, no appreciable small ice crystals ($r_i < 5 \, \mu m$) can be found for either the mass content or the number concentration fields. So, the discussion will be focused on the other three types of ice particles.

Figures 4.26 and 4.27 show the mass content and number concentration fields, respectively, for planar ice particles in the clouds. The planar ice particles appear between the -10 and -20°C level in the Sierra cloud, with a maximum mass content of 0.4 g m$^{-3}$ at 63 km HMD and 4.4 km MSL. At about 65 km HMD, where the motion of the air above 3.5 km MSL is downward, the planar crystal vanishes due to evaporation. One can notice that a small amount of the planar crystals appears near the ground at about 65 to 75 km HMD. These low-altitude planar crystals occur at levels with temperatures above -4 °C, and are not likely to be formed locally. They are actually moderately rimed planar crystals falling through from the higher levels. Some trace amount of planar crystals can also be found at the lower altitudes at 85 to 100 km and 120 to 135 km HMD. The maximum number concentration of the planar crystals, as
Figure 4.26: Planar ice mass content in the simulated orographic cloud. Contour interval is 0.05 g m$^{-3}$.

Figure 4.27: Planar ice number concentration in the simulated orographic cloud. Contour interval is 0.1 per liter.
shown in Figure 4.27, is above one per liter. The number concentrations for those low-altitude crystals are very low.

Notice that, in contrast to the Sierra cloud, there is no significant amount of ice formed in the Carson cloud. Two possible factors are likely to be responsible for such a result. First, potential ice nuclei could be lost due to ice nucleation or could be captured by liquid drops. The latter is most effective in the downdraft region where evaporation occurs. Thus, there might not be enough ice nuclei left as the air enters the Carson cloud. Also, the effects of condensation and sedimentation remove water vapor from the upper air. This drying-out effect means a reduction in the degree of supersaturation (which is critical to the ice nucleation) that can be acquired when the air later reaches a temperature level that was previously suitable for ice nucleation.

Figures 4.28 and 4.29 show the mass content and number concentration fields, respectively, for columnar ice particles. The mass content of columnar ice is quite low, with a maximum of 0.026 g m$^{-3}$ at 30 km HMD and 3.6 km MSL (Figure 4.28). The columnar ice particles were first formed at temperatures above -10 °C, but are then advected upward with the air to the layers where the temperatures are just below -10 °C, which is the planar crystal habit regime. The shaded area indicates the region of the planar crystals that was shown previously. The columnar ice crystals are formed at higher temperatures than that for the planar crystals.

The maximum number concentration of columnar crystals is less than 0.3 per liter, which occurred at 22 km HMD and 3.5 km MSL (Figure 4.29). The number concentration of the columnar crystals is lower than that of the planar crystals, mainly because the degree of supersaturation in mixed-phase clouds is normally lower at the higher temperatures. Lower supersaturation usually means a lower nucleation rate, as was discussed in Section 2.3.1.1 and Section 4.3.
Figure 4.28: Columnar ice mass content in the simulated orographic cloud. Contour interval is 0.05 g m$^{-3}$. The shaded area indicates the region of significant amount planar ice in Figure 4.26.

Figure 4.29: Columnar ice number concentration in the simulated orographic cloud. Contour interval is 0.1 per liter. The shaded area indicates the region of significant number of planar ice in Figure 4.27.
Figures 4.30 and 4.31 show the mass content and number concentration fields, respectively, for the graupel particles. The mass content of graupel has a maximum of over 0.2 g m\(^{-3}\) at 62 km HMD and 4.0 km MSL. The top of the graupel area coincides with the top of the cloud water area (where riming may occur). There is also some graupel formed near the ground, with a maximum mass content of over 0.15 g m\(^{-3}\) at 70 km HMD. This lower-level graupel area is located at the same area of relatively high liquid water content -- a potential area for riming to take place.

The number concentration of graupel has maxima of over 0.3 per liter at 40 km HMD and 3.7 km MSL, as well as at 55 km HMD and 3.9 km MSL. Note the position of the planar crystals (light-shaded area) and columnar crystals (dark-shaded area) relative to the field of graupel. The area of graupel is just downwind of the columnar crystal area. Since no columnar crystals are found shortly after the air trajectories enter the graupel zone, it is likely that the columnar crystals are transformed into graupeln. However, since the maximum number concentration of graupeln is higher than that of the columnar crystals, at least some of the graupeln probably originated from the planar crystals. The number concentration of graupel near the ground is very low. It is reasonable to assume that these graupel particles are relatively large in size if one compares the low number concentrations with the relatively high mass contents.

The complete microphysical structure of the simulated clouds is shown in Figure 4.32 for cloud condensates of mass content greater than 0.05 g m\(^{-3}\). The Sierra cloud extended over 100 km horizontally and had a maximum depth of 4 km. It had a pure ice zone (predominantly planar ice), mixed-phase zones, and supercooled liquid-phase zones. The Carson cloud extended over 30 km horizontally and had a maximum depth of about 2 km. The simulated cloud is composed of mostly supercooled liquid drops.
Figure 4.30: Graupel mass content in the simulated orographic cloud. Contour interval is 0.05 g m\(^{-3}\). The light and dark shaded area indicate the regions of significant amount of planar ice and columnar ice, respectively.

Figure 4.31: Graupel number concentration in the simulated orographic cloud. Contour interval is 0.1 per liter. The light and dark shaded areas indicate regions of significant amount of planar ice and columnar ice, respectively.
Figure 4.32: Complete microphysical structure of the simulated orographic cloud. The different particle fields are cloud drops (C), drizzle/rain (D), planar ice (P), columnar ice (N), and graupel (G).
**Aerosol particle fields**

Figure 4.33 shows the number concentration of total cloud condensation nuclei (CCN), including those that initiated the cloud and drizzle/rain drops. Following the air trajectories, one finds that the number concentration of CCN should decrease only slightly outside of the cloud, due to the expansion of air. However, the number concentration of CCN decreases drastically in the zone of drizzle/rain (cf. Figure 4.25), an indication of the reduction of drop number due to coalescence. Figure 4.34 shows the number concentration of inactivated CCN particles -- haze particles in the clear air and interstitial particles in the cloud (i.e., Figure 4.33 without cloud and drizzle/rain drops). Following the air trajectories this time, one finds that the decrease in the particle number concentration occurs at much earlier times. In fact, the line of distortion in the contours that extended from the upper left (14 km HMD, 3 km MSL) to the lower middle (50 km HMD, 1.5 km MSL) indicates the cloud base boundary. Again, the particle number concentration decreases as air passing through the drizzle/rain zone. In subsaturated air, cloud drops will evaporate and return to the inactivated drop population, as indicated by the increase of particle number concentration just above the Lake Tahoe Valley. For the layer of air nearest to the ground, the aerosol particle concentration is modified by the cloud from a value of 500 cm\(^{-3}\) at 0 km HMD to about 200 cm\(^{-3}\) in the Lake Tahoe Valley.
Figure 4.33: Number concentration of the total CCN particles in the simulation. Contour interval is 25 cm\(^{-3}\).

Figure 4.34: Number concentration of inactivated CCN particles in the simulation. Contour interval is 25 cm\(^{-3}\).
Precipitation fields

The simulated precipitation rates on the ground are shown in Figure 4.35. The liquid-phase precipitation (dash-lines, mainly drizzle) from the Sierra cloud falls over a broad distance between 65 and 115 km HMD, with a maximum rate of 0.04 mm hr\(^{-1}\). Also, drizzle from the Carson cloud can be found at between 130 and 150 km HMD, with a maximum precipitation rate of 0.02 mm hr\(^{-1}\). In contrast to liquid-phase precipitation, the ice-phase precipitation (thick-lines) appears mainly in a narrow range between 68 and 76 km HMD from the Sierra cloud, with a maximum rate of 0.4 mm hr\(^{-1}\). The cut-off of the ice-phase precipitation is mainly due to the dissipation of the high-level ice zone in the downdraft region. The particles in this precipitation event are mostly graupel. Some very light ice-phase precipitation can also be found at 125 to 130 km HMD from the Carson cloud, with a rate of merely 2x10\(^{-6}\) mm hr\(^{-1}\). The ice crystals falling from the Carson cloud are just slightly rimed. These low precipitation rates are not uncommon for wintertime, orographic clouds, despite that there is plenty of condensed water in the cloud. Since most of the liquid particles in the cloud are supercooled, it is possible to introduce ice particles at the right location to enhance the precipitation. Cloud seeding experiments, such as the Sierra Cooperative Pilot Project, are used to increase the precipitation rates from such clouds.
Figure 4.35: Precipitation rates in the simulation. The dash-lines are for the liquid-phase precipitation and the thick-lines are for the ice-phase precipitation.
4.4.3. Chemical Properties and the Relative Removal Efficiencies

In this section, two parameters are introduced for the discussion of the redistribution of atmospheric trace chemicals through cloud processes. The mass ratios (MR) are each defined as the ratio of the mass of trace chemicals in a certain phase at any particular time and space to that in the initial air parcel. The relative removal efficiencies (RRE) are each defined as the ratio of the removal efficiency of each trace chemical species to that of water vapor (see Section 4.1 for details). For the relative removal efficiencies, we are not considering the temporal removal of chemicals in the gas-phase into the condensed phase, which still remains in the air. Only the precipitation "on the ground" is considered.

Chemical mass ratios

The four chemical species considered here are water, S(IV), sulfate, and hydrogen peroxide. We will discuss the mass ratios (1) in the liquid-phase, (2) in the ice phase, and (3) the total (gas-, liquid- and ice-phases) compared with total mass in the original air parcel. Trace chemicals such as CO$_2$ and O$_3$ that are not interactive with the cloud particles will be neglected in the discussion.

Figure 4.36 shows the fraction of the original water vapor that is in the liquid-phase. The distribution of the MR for liquid water is quite similar to that of the mass contents of cloud drops, except that the maxima are somewhat higher in altitude. The difference in the positions of the maxima is a result of the temperature dependence of the saturation ratio, because more water can be condensed out at lower temperatures. The maximum MR of liquid water is near 20% at about 3.5 km MSL for both the Sierra cloud and the Carson cloud. Figure 4.37 shows the fraction of the original water vapor
Figure 4.36: Mass ratio of water in the liquid-phase to the original total water.

Figure 4.37: Mass ratio of water in the ice-phase to the original total water.
that is in the ice particles. The maximum MR of ice water is 26% at 60 km HMD and 4.5 km MSL above the liquid-phase zone.

Figure 4.38 shows the MR for the total water in the air. Note that the deviation of the MR for the total mass of a certain species reflects the removal of that species from the air, usually by means of sedimentation. Also, one can estimate the depletion rate by looking at the gradient of the MR contours along the air trajectories. There are generally two major water depletion zones. The upper level zone is at 65 to 75 km HMD and near 4 km MSL, where the maximum of the graupel field is. The lower level one is at about 70 to 100 km at the lowest 1.5 km cloud depth, where drizzle/rain, as well as some graupeln, are formed.

Figure 4.38: Mass ratio of total water to the original total water.
Figures 4.39 through 4.41 show the MR for the S(IV) species. The distribution of the MR for S(IV) in the liquid-phase is very similar to that of water (Figure 4.36). The maximum MR is over 6% for both the Sierra and Carson clouds. At the same location, the MR of liquid water is less that 20%. Note that the MR of a chemical species to that of water can be called the "potential relative removal efficiency", since the cloud particles can potentially be removed from the atmosphere. The potential RRE for S(IV) is about 0.3 at the location of the maximum MR for S(IV). The MR for S(IV) in the ice-phase has a maximum of about 0.6 % (Figure 4.40), which is an order of magnitude lower than that in the liquid-phase. Figure 4.41 shows the MR for total S(IV) in the air. S(IV) is generally not significantly removed in the ice-phase zone. The removal is limited within the lowest 2 km of the cloud. Note the shaded area actually has a surplus in total S(IV). The increase of total S(IV) occurs at the entrance of that shaded area (65 to 75 km HMD) as a result of the out-gassing of SO₂ during the riming process.

Figure 4.39: Mass ratio of S(IV) in the liquid-phase to the original total S(IV).
Figure 4.40: Mass ratio of S(IV) in the ice-phase to the original total S(IV).

Figure 4.41: Mass ratio of total S(IV) to the original total S(IV).
Figures 4.42 through 4.44 show the MR for the sulfate, the S(VI) species. This sulfate field can also represent the MR for the N(III) species, which is also one of the major component of the ammonium sulfate CCN particles in the model. Note that haze particles and interstitial aerosol particles are both considered to be in the liquid-phase particle category. Since all sulfate is initially in the haze particles, the MR for sulfate in the liquid-phase is near unity in the beginning. As shown in Figure 4.42, the decrease of the liquid-phase sulfate occurs at two locations, where the MR gradient along the air trajectories is large. The first one occurs at 30 to 65 km HMD and 4 km MSL, mainly resulting from the collection of liquid drops by ice particles, and (2) 60 to 80 km HMD at the lowest 1.5 km, due to both riming and fallout. The minimum amount of sulfate remaining in the liquid phase can be as little as 10% of its original value. The shaded area indicates where there is an increase of the liquid-phase sulfate due to sedimentation of drops from above. Figure 4.43 shows the MR for ice-phase sulfate, which coincide with the graupel fields. It is not surprising that these two fields are similarly located since the major route for ice particles to acquire sulfate is through the accretion of liquid drops. The maximum MR for sulfate in the ice is over 50%. Compared with the 26% maximum MR for ice water, sulfate may actually be removed more efficiently than water by ice particles. Figure 4.44 shows the MR for total sulfate. The large gradients along the air trajectory generally coincide with the area of large particles (graupel and drizzle/rain). The total sulfate can be depleted to less than 20% of its original values. A maximum increase of 80% (65 km HMD, 1.2 km MSL) could also happen due to a positive net flux of cloud particles sedimenting from the upper levels.
Figure 4.42: Mass ratio of sulfate in the liquid-phase to the original total sulfate.

Figure 4.43: Mass ratio of sulfate in the ice-phase to the original total sulfate.
Figures 4.45 through 4.47 show the MR for the H$_2$O$_2$ species. As can be seen in Figure 4.45, H$_2$O$_2$ is highly soluble in the liquid. Most of the liquid cloud area can take up more than 50% of the total H$_2$O$_2$. The shaded area at 66 km HMD and 1.2 km MSL indicates the effect of sedimentation. Figure 4.46 shows the MR for H$_2$O$_2$ in the ice-phase. Since sorption of H$_2$O$_2$ gas onto the ice is not considered in this simulation, H$_2$O$_2$ can be incorporated into ice only by the accretion of liquid drops that contain dissolved H$_2$O$_2$. The maximum MR for H$_2$O$_2$ is about 22% at 64 km HMD and 4 km MSL, which is comparable to that of water. However, the MR for H$_2$O$_2$ in the graupel field near the ground (maximum of 16%) is much higher that of water (<0.04%) at the same location. Figure 4.47 shows the MR for total H$_2$O$_2$. Similar to the sulfate species, the contour gradient for H$_2$O$_2$ along the air trajectories is largest at the lower levels at 65 to 90 km HMD. The total H$_2$O$_2$ in the air can be depleted to less than 20% of its original values. A maximum increase of 40% (68 km HMD, 1.2 km MSL) could also happen due to a positive net flux of cloud particles falling from the upper levels.
Figure 4.45: Mass ratio of H$_2$O$_2$ in the liquid-phase to the original total H$_2$O$_2$.

Figure 4.46: Mass ratio of H$_2$O$_2$ in the ice-phase to the original total H$_2$O$_2$. 
Figure 4.47: Mass ratio of total H$_2$O$_2$ to the original total H$_2$O$_2$.
Relative removal efficiencies

From the formula (4.3) given in Section 4.1, the relative removal efficiencies (RRE) of various trace chemicals are calculated by comparing the species concentration in the precipitation (collected on the ground) to that in the lowest level of the original air parcel. Figure 4.48 shows the RRE in the liquid-phase precipitation. Sulfate and $\text{H}_2\text{O}_2$ can be removed more effectively than water from the atmosphere by precipitation. At the onset of liquid-phase precipitation (60 km HMD), the RRE for sulfate and $\text{H}_2\text{O}_2$ can be as high as 300 and 50, respectively. This means sulfate (respectively $\text{H}_2\text{O}_2$) can be removed from the atmosphere 300 (50) times more effectively than water. At further distances, the precipitation rate increases, which means the liquid water content in the air also increases. Therefore, the RRE drops as a result of the dilution effect. One can observe the anti-correlation between the precipitation rate and the RRE for sulfate and $\text{H}_2\text{O}_2$. The RRE of the Carson cloud liquid-phase precipitation for sulfate and $\text{H}_2\text{O}_2$ is generally lower than that of the Sierra cloud, which reflects the relatively high liquid water content and low CCN concentrations in the Carson cloud. The solubility of $\text{SO}_2$ is controlled by the pH value in the liquid. Since the pH value in the liquid is lower when the liquid water content is low, one can expect a positive correlation between the precipitation rate and the RRE for $\text{SO}_2$. The RRE for $\text{SO}_2$ is around 0.01 to 0.3. Thus, $\text{SO}_2$ can be removed less effectively than water in the precipitation. The removal of the insoluble species by precipitation is very ineffective. The RRE for $\text{CO}_2$ is about $7\times10^{-6}$, and for $\text{O}_3$ it is about $2\times10^{-6}$.

Figure 4.49 shows the RRE in the ice-phase precipitation. There are basically three types of ice-phase precipitation, as reflected by the variation of the RRE for various chemical species. The first type is the highly rimed (graupel) particles, as indicated by the first shaded area at between 70 to 76 km HMD. The RRE for sulfate and $\text{H}_2\text{O}_2$ for
Figure 4.48: The relative removal efficiencies for the liquid-phase precipitation.

Figure 4.49: The relative removal efficiencies for the ice-phase precipitation.
this type of ice particle are about 2 to 10, and for SO$_2$ they are about 0.004 to 0.04. The RRE for CO$_2$ and O$_3$ are negligible in ice-phase precipitation. The time variations of the RRE in the highly rimed ice are opposite to those in the liquid-phase precipitation. The RRE for sulfate and H$_2$O$_2$ are now positively correlated with the precipitation rates of ice particles. Since there is essentially no sulfate or H$_2$O$_2$ in the unrimed ice (sorption of H$_2$O$_2$ on ice is not treated here), it is likely that the higher ice-precipitation rates are associated with a higher degree of riming. However, SO$_2$ can be incorporated into ice without riming. As shown in Section 4.1, the concentration of SO$_2$ in the depositional ice is higher than that in the rime ice at temperatures above -11°C. Since the riming mostly occurs at the lowest 1.5 km of the cloud, where the drizzle/rain and cloud drop contents are high, it is natural that the RRE for SO$_2$ should be higher in the less-rimed ice. In fact, it can be seen that the RRE for SO$_2$ in the ice-phase precipitation, which is mostly unrimed, at 78 to 102 km HMD, as well as at 122 to 142 km, is somewhat higher that in the rime ice. Note that the precipitation rate for the unrimed events is so low that they are off the scale in Figure 4.35. The RRE for SO$_2$ in the unrimed ice is about 0.1, which is within a factor of 3 of the maximum of that in the liquid-phase. In the event of slightly rimed ice precipitation (128 to 130 km HMD), as indicated by the shaded area on the right, the RRE for SO$_2$ is similar to that for the unrimed ice while the RRE for sulfate and H$_2$O$_2$ are much less than that in the highly rimed ice. Figure 4.50 shows the RRE in the combined liquid- and ice-phase precipitation. The curves are basically the same as those for the liquid-phase RRE, except when there is major ice-phase precipitation taking place. The ice-phase precipitation generally decreases the RRE for all chemical species.
Figure 4.50: The relative removal efficiencies for the total precipitation.
4.4.4. Summary

The simulation presented in this section revealed some detailed microphysical structures of the winter-time, orographic clouds. Distinct zones of cloud drops and drizzle, as well as ice-phase particles with different growth habits, are shown to exist in the clouds. Regions that are purely ice-phase, mixed-phase, or supercooled liquid-phase are present in the clouds. The precipitation from these simulated clouds is relatively weak. The effects of cloud processes on the spatial redistribution of various trace chemicals have also been demonstrated. The concept of the relative removal efficiencies, which was tested with a simple particle model (Section 4.1), is now reexamined with this more complete cloud-scale model. The results are in good agreement with those from the simple particle model.

A fair comparison between the current model results and actual observations cannot be made as yet. Some observational studies have been done on similar cases (Deshler et al., 1990), but they are mainly cloud seeding experiments. Nevertheless, the general microphysical structures of the simulated and the observed clouds are quite similar, except that there tends to be more precipitation produced in the cloud seeding experiments. It would be interesting to do a cloud seeding simulation with the model and compare the detailed microphysical structures with observations in the future.
Chapter 5

CONCLUSIONS

5.1. Summary

A multi-component, multi-phase model has been developed to study the effects of cloud microphysical processes on the redistribution of atmospheric trace substances. A hybrid bin-method, which is similar to the method-of-moments scheme, is applied in the multi-component particle framework to ensure fast and accurate calculation of the particle growth. The multi-component particle framework categorized the distribution of liquid-phase particles according to their water and solute masses. An additional shape factor (aspect ratio) was applied to the categorization of ice-phase particles.

The liquid- and ice-phase microphysical processes have been treated in detail in this study. In addition, a set of basic liquid-phase chemical processes was included without using the assumption of equilibrium between the gas- and liquid phases. Special efforts have been put on the growth and habits of the ice crystals. Through a theoretical approach, it was found that the growth habits of ice crystals are mainly controlled by three distinct factors. The first factor is the inherent growth ratio that is determined by the surface kinetic processes and is a function of temperature only. The second factor is the distortion of vapor density fields due to the asymmetrical shape of the ice crystals; this factor can be expressed as a function of the aspect ratio of the ice crystals. The third factor is the ventilation effect, which is a function of the size and shape of the ice crystals. With the help of these three factors, a parameterization scheme for the growth habits of ice crystals was developed that yields good agreement
with observational data. Some recent laboratory results on the ice-phase chemical processes (sorption and entrapment) were also parameterized and included in the model. Results from the earlier stage of this study showed that the drop number concentration is a function of both the water mass and the solute mass in the drops, a phenomenon that cannot be resolved by conventional cloud models. After applying the complete microphysics in a parcel model, it was also shown that the number concentration of ice particles is indirectly controlled by the number concentration of cloud condensation nuclei. Bulkwater models that cannot treat the in-cloud supersaturation are not able to simulate such processes properly.

The concept of relative removal efficiency (RRE), a measure of the ability of a chemical species to be removed in the precipitation compared to that of water, was introduced and tested in a simple particle model in the earlier stage of the study. An extended test on the RRE was done by simulating a wintertime, orographic cloud with the complete model. Satisfactory results for both the microphysical and chemical behavior of the cloud were produced in the simulation. It was shown that the redistribution of the atmospheric trace substances is controlled by their microphysical pathways. The RRE in the liquid-phase precipitation ranged from 1 to 300 for sulfate, from 0.01 to 0.3 for S(IV), from 1 to 50 for H$_2$O$_2$, and it is about 8x10$^{-6}$ for CO$_2$, and 3x10$^{-6}$ for O$_3$. The variations of the liquid-phase RRE are controlled mainly by the amount of liquid water in the air and the pH values in the liquid drops. The RRE in the ice-phase precipitation is about 0.006 to 10 for sulfate, 0.04 to 0.1 for S(IV), and 0.004 to 5 for H$_2$O$_2$. The variations of the ice-phase RRE are mainly controlled by the rimed mass fraction in the ice particles. The RRE for CO$_2$, and O$_3$ are negligible in the ice-phase precipitation. In the simulated wintertime, orographic clouds, the maximum mass fractions that can be removed from the air parcel are > 20% for water vapor, 5% for SO$_2$, > 90% for sulfate
and N(III), and > 90% for H₂O₂. The number concentrations of cloud condensation nuclei can be reduced to less than 40% of their original values.

The development of the detailed microphysical and chemical cloud model for the study of cloud processes was successful. Some recent experimental data for the ice-phase chemical processes, which are generally ignored in traditional cloud models, was included in this study. The goal of studying the effect of cloud processes on the redistribution of atmospheric trace chemicals was accomplished by applying this cloud model to the simulation of orographic clouds. It has been shown that cloud processes are can be important to the budgets of the atmospheric trace substances.

5.2. Future Perspectives

The current knowledge of the liquid-phase microphysics seems to be fairly sufficient. However, there are still some unexplained discrepancies between the results from the numerical simulations and those from observations. For instance, the calculated cloud drop size distributions are normally quite narrow, as shown in Section 4.2, while the observed distributions are broader. Such inconsistency is probably not due to bad microphysics in the numerical simulation, but rather caused by some overlooked factors. One of the factors might be the mixing or entrainment of dry air into the cloud. Also, since the saturation ratio is largely controlled by the updraft velocity, the small-scale turbulence in the cloud may cause drops in the same vicinity to experience different supersaturations. Therefore, drops with the same properties do not necessarily have the same growth rate in one grid cell. Such a phenomenon is not resolvable in typical cloud models that have grid sizes on the order of a hundred meters and that use a constant saturation ratio across each grid space. However, instead of tracking only the mean saturation ratio, one could assume that the saturation ratio has some type of subgrid
distribution (e.g., normal or Gaussian). The mean of the distribution is simply the mean saturation ratio that the models keep track of, whereas the spread of the distribution could be determined empirically from the magnitude of the small-scale turbulence or the degree of mixing. Such distribution functions could then be incorporated into the condensational growth equation to account for the inhomogeneity of the saturation ratio within a single grid cell. This approach can even be applied to other subgrid phenomena.

Although the treatment of microphysics in this study is very detailed, there is still much room for improvement. Due to inadequate knowledge, some of the important ice-phase processes have been ignored. For instance, there is little information available on the shape and density of ice-crystal aggregates and fragments. Nevertheless, it is possible to obtain the shape and density of snow aggregates from field observation. It is also feasible to apply fractal theory to describe the shape of snow aggregates. Extended studies on aggregation and other ice-phase processes will be very useful to simulations of this kind. In the present study, the potential ice nuclei were assumed to be monodispersed. However, the size of the IN is an important factor for calculating the rates of deposition and contact nucleation. It would be instruction to apply a categorized size distribution for the ice nuclei in the future.

The simulations in Section 4.2 have shown that the drop distribution is multi-dimensional. Drops of the same sizes may contain different amounts of solute. However, the effect of the variation of solute concentration on the chemical reactions was not studied. It would be a good topic to compare the results from this model against those from a bulk-water type model for analyzing the nonlinear dependence of the chemical reactions on the solute content.

This model has been successfully used in testing some laboratory results of the ice-phase chemistry. Such efforts should be continued to test upcoming laboratory or
theoretical results. Also, since this model provides detailed particle size and shape distributions, a comparison of the size- and shape-related parameters should be invaluable for the verification of the model results with remote-sensing measurements. Furthermore, the information about the size and shape distributions gained from this model can be used in the calculation of radiative transfer in either cirrus clouds or large-scale stratiform clouds, which are very important to the global radiation budgets.

The strength of this multi-component bin model is its ability to give detailed descriptions of the microphysical and chemical processes. Yet, it is also too time-consuming to be implemented directly in a mesoscale model at the present stage. A good use of this model would be to use the statistical approach of Lee (1990) to produce "bulk-water parameterizations" that can be used in meso- or large-scale models. Such microphysical parameterizations are physically based and are more efficient than the Marshall-Palmer type parameterizations. With the concept of the relative removal efficiency, we can also use the model to provide chemical parameterizations that can be applied to the calculations of trace chemical removal in meso- and large-scale models.

The final simulation of this study was done on a case of wintertime, orographic cloud formation. The precipitation efficiencies in such clouds are often relatively low, so it is not uncommon for cloud seeding experiments to be conducted. It would be instructional to run the same case with artificial seeding. Such simulations could be very useful for developing targeting strategies in real cloud seeding programs.

The detailed microphysical and chemical model developed here has been shown to be very useful in the study of cloud processes. However, this model should be improved further and applied in various fields of atmospheric sciences whenever clouds are involved.
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Appendix A

LIST OF SYMBOLS
### LIST OF SYMBOLS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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<tr>
<td>(a)</td>
<td>drop radius</td>
<td>[m]</td>
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<tr>
<td>(a)</td>
<td>semi-major axis of oblate spheroid</td>
<td>[m]</td>
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<td>(a_w)</td>
<td>activity of liquid water in solution</td>
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<td>(a_v)</td>
<td>activity of water vapor in air</td>
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<tr>
<td>(c)</td>
<td>specific heat capacities:</td>
<td>[J kg(^{-1}) K(^{-1})]</td>
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<tr>
<td>(c_v)</td>
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<td>(c_{vd})</td>
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<td>(c_{v_v})</td>
<td>for water vapor (= 1390 at STP)</td>
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<td>(c_{pd})</td>
<td>for dry air (= 1005 at STP)</td>
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</tr>
<tr>
<td>(c_{pv})</td>
<td>for water vapor (= 1850 at STP)</td>
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<tr>
<td>(c_i)</td>
<td>specific heat capacity of ice = 2106 + 7.327 (T_c)</td>
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</tr>
<tr>
<td>(c_w)</td>
<td>specific heat capacity of liquid water</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(= 4178 + 1.298 \times 10^{-2} (T_c - 35)^2 + 1.591 \times 10^{-5} (T_c - 35)^4) for (T_c &gt; 0) °C</td>
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<tr>
<td></td>
<td>(= 4218 + (-11.326 - 0.09728(-0.018329 + 1.1361 \times 10^{-3} T_c) T_c)T_c T_c) for (T_c \leq 0) °C</td>
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<td>(c)</td>
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</tr>
<tr>
<td>(C_D)</td>
<td>hydrodynamic drag force coefficient</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(</td>
<td>D</td>
</tr>
<tr>
<td>(C)</td>
<td>electrostatic capacitance analogy for the diffusional growth of ice crystal</td>
<td>[m]</td>
</tr>
<tr>
<td>(d)</td>
<td>diameter</td>
<td>[m]</td>
</tr>
<tr>
<td>(d)</td>
<td>length of foci of an ellipse</td>
<td>[m]</td>
</tr>
</tbody>
</table>
D drop diameter [m]
diffusivities, diffusion coefficients: [m² s⁻¹]

\(D_v\) diffusivity of water vapor in air = \(2.11 \times 10^{-5} \left(\frac{T}{T_o}\right)^{1.94} \left(\frac{P_o}{P}\right)\)

\(D_p\) diffusivity for small particles in air = \(\frac{k T_o \rho_c}{6 \pi r_p \eta}\)

hydrodynamic drag forces: [N]

\(D_{Os}\) Oseen flow drag = \(6 \pi r_p \eta V_\infty \left(1 + \frac{3}{16} N_{Re}\right)\)

\(D_S\) Stokes flow drag = \(6 \pi r_p \eta V_\infty\)

e vapor pressures: [Pa]

\(e_{s,i}\) saturation vapor pressure over ice

\[e_{s,i} = 610.78 + 50.347 T_c + 1.8860 T_c^2 + 4.1762 \times 10^{-2} T_c^3 + 5.8247 \times 10^{-4} T_c^4 + 4.8388 \times 10^{-6} T_c^5 + 1.8388 \times 10^{-8} T_c^6\]

for \(-50 \leq T_c \leq 0\) °C

\(e_{s,w}\) saturation vapor pressure over water

\[e_{s,w} = 610.78 + 44.365 T_c + 1.4289 T_c^2 + 2.6506 \times 10^{-2} T_c^3 + 3.0323 \times 10^{-4} T_c^4 + 2.0341 \times 10^{-6} T_c^5 + 6.1368 \times 10^{-9} T_c^6\]

for \(-50 \leq T_c \leq 50\) °C

\(E_c\) collection efficiency

E collision efficiencies:

\(E_{colli}\) collision efficiency

\(E_{coal}\) coalescence efficiency

\(E_{brk}\) breakup efficiency

\(E_{reb}\) rebound efficiency

E energies: [J]

\(E_T\) total energy of coalescence

\(E_{CKE}\) collision kinetic energy

f ventilation coefficients:

\(f_h\) heat ventilation coefficient in air

\[f_h = 1 + 0.108 N_{Re} N_{Pr}^{2/3}\]

for \(N_{Re} N_{Pr}^{1/3} < 1.4\)

\[f_h = 0.78 + 0.308 N_{Re}^{1/2} N_{Pr}^{1/3}\]

for \(N_{Re} N_{Pr}^{1/3} \geq 1.4\)

\(f_v\) mass ventilation coefficient of water vapor

\[f_v = 1 + 0.108 N_{Re} N_{Sc,v}^{2/3}\]

for \(N_{Re} N_{Pr}^{1/3} < 1.4\)

\[f_v = 0.78 + 0.308 N_{Re}^{1/2} N_{Sc,v}^{1/3}\]

for \(N_{Re} N_{Pr}^{1/3} \geq 1.4\)
\[ f_p = \text{mass ventilation coefficient of aerosol particles in air} \]
\[ = 1 + 0.3N_{Re}^{1/3}N_{Sc,a}^{1/3} \]

\[ f \]
\[ f_{Cu} = \text{Cunningham slip-flow correction} = 1 + \alpha N_{Kn} \]
\[ f_{df} = \text{correction factor in diffusiophoretic correction equation} = 0.85 \sim 1.0 \]
\[ f_{kin} = \text{correction factor of the kinetic effect for depositional growth} \]
\[ = \left[ \frac{r}{r + \Delta} + \frac{D_v}{\alpha_e r \sqrt{R_v T_\infty}} \right]^{-1} \]
\[ f_{prx} = \text{source and sink proximity correction factor for depositional growth} \]
\[ f_{th} = \text{correction factor in thermophoretic correction equation} \]
\[ = \frac{0.4 f_{Cu} (k_a + 2.5 k_p N_{Kn})}{(1 + 3 N_{Kn}) (2 k_a + 5 k_p N_{Kn} + k_p)} \]
\[ f_{ent} = \text{entrainment factor} \]
\[ f_{sor} = \text{sorption factor} \]
\[ \Delta F_{act} = \text{activation energy for the self diffusion of liquid water to form ice embryo} \quad [J] \]

\[ g = \text{normal acceleration of gravity} = 9.80665 \quad [m \text{ s}^{-2}] \]
\[ g = \text{generation rate in a first-order rate equation} \]
\[ G = \text{gravitational constant} = 6.67 \times 10^{-11} \quad [N \text{ m}^2 \text{ Kg}^{-2}] \]
\[ G = \text{Gibbs free energy} \]
\[ \Delta G = \text{critical energy for ice embryo to freeze} \quad [J] \]

\[ h = \text{Planck’s constant} = 6.6252 \times 10^{-34} \quad [J \text{ s}] \]
\[ h = \text{specific total heat} \quad [J \text{ mol}^{-1}] \]
\[ h = \text{specific enthalpy} \quad [J \text{ mol}^{-1}] \]
\[ H = \text{Henry’s law coefficients}:: \]
\[ H_{NH_3} = \text{Henry’s law coefficient for ammonium} \]
\[ H_{CO_2} = \text{Henry’s law coefficient for CO}_2 \]
\[ H_{SO_2} = \text{Henry’s law coefficient for SO}_2 \]
\[ H_{O_3} = \text{Henry’s law coefficient for O}_3 \]
\[ H_{H_2O_2} = \text{Henry’s law coefficient for H}_2\text{O}_2 \]
\[ H = \text{total heat} \quad [J] \]
\( H \) enthalpy \([J]\)

\( i_s \) vant Hoff’s dissociation coefficient

\( \mathbf{J} \) mass flux \([\text{Kg m}^{-2} \text{s}^{-1}]\)

\( J_{HF} \) homogeneous freezing rate \([\text{s}^{-1}]\)

\( J_{\text{splinter}} \) rime-splintering rate \([\text{s}^{-1}]\)

\( k \) Boltzmann’s constant \(= 1.38062 \times 10^{-23} \) \([\text{J K}^{-1}]\)

rainout frequency \([\text{s}^{-1}]\)

\( \kappa \) thermal conductivities: \([\text{W m}^{-1} \text{K}^{-1}]\)

\( \kappa_a \) for air \(= 2.3823 \times 10^{-2} + 7.1177 \times 10^{-5} T_c \)

\( \kappa_p \) for aerosol particle

\( \kappa_w \) for water \(= 0.561 + 1.683 \times 10^{-3} T_c \)

\( \kappa \) thermal diffusivity \(\kappa = \frac{k}{\rho c}\) \([\text{m}^2 \text{s}^{-1}]\)

\( \xi \) characteristic frequency \(= 1/\tau\) \([\text{s}^{-1}]\)

\( K \) collection kernels: \([\# \text{m}^3 \text{s}^{-1}] \text{ or } [\# \text{mol s}^{-1}]\)

\( K_{\text{ac}} \) ice accreting droplets

\( K_{\text{bk}} \) collision-breakup

\( K_{\text{Br}} \) Brownian diffusion collection

\( K_{\text{co}} \) collision-coalescence collection

\( K_{\text{df}} \) diffusiophoretic collection

\( K_{\text{th}} \) thermophoretic collection

dissociation coefficients:

\( K_{a1} \) first dissociation coefficient of ammonium \([\text{M}], [\text{mol m}^{-3}]\)

\( K_{c1} \) first dissociation coefficient of C(IV) \([\text{M}], [\text{mol m}^{-3}]\)

\( K_{c2} \) second dissociation coefficient of C(IV) \([\text{M}], [\text{mol m}^{-3}]\)

\( K_{s1} \) first dissociation coefficient of S(IV) \([\text{M}], [\text{mol m}^{-3}]\)

\( K_{s2} \) second dissociation coefficient of S(IV) \([\text{M}], [\text{mol m}^{-3}]\)

\( K_w \) dissociation coefficient of water \([\text{M}^2], [\text{mol}^2 \text{m}^{-6}]\)
specific heats of change of state (latent heat): \[[J \text{ Kg}^{-1}]\]

- \(L_f\) latent heat of freezing = 0.3337 \times 10^6 + (2031. - 10.467 T_c) T_c
- \(L_v\) latent heat of vaporization = 2.5008 \times 10^6 (T_o/T)^{(0.167+3.67 \times 10^{-4} T)}
- \(L_s\) latent heat of sublimation = \(L_f + L_s\)

molar specific heats of the change of state = \(L / M_w\): \[[J \text{ mol}^{-1}]\]

- \(l_f\) molar heat of freezing
- \(l_v\) molar heat of vaporization
- \(l_s\) molar heat of sublimation = \(l_f + l_s\)

mass \[[\text{ Kg}]\text{ or [mol]}\]

molecular weights: \[[\text{ g mol}^{-1}]\]

- \(M_d\) molecular weight of dry air = 28.9644
- \(M_w\) molecular weight of water vapor = 18.0160

first moment of a distribution function

number of moles of molecules \[[\text{ mole}]\]

number density function

number density of ice embryo in drops \[[\# \text{ Kg}^{-1}]\]

concentration of species \(j\) in the air \[[\text{ mol m}^{-3}]\]

numbers and number concentrations:

- \(N_A\) Avogadro number = 6.022169 \times 10^{23} \[[\text{ molec mol}^{-1}]\]
- \(N_{CON}\) number of cloud condensation nuclei \[[\# \text{ mol}^{-1}]\]
- \(N_{IN}\) number of ice forming nuclei \[[\# \text{ mol}^{-1}]\]
- \(N_{Bo}\) Bond number = \(g (\rho_w-\rho_a) r^2 / \sigma_{w,a}\)
- \(N_{Da}\) Davies number = Best number = \(C_D N_{Re}^2 = \frac{32 r^3 (\rho_w-\rho_a) \rho_a g}{3 \eta^2}\)
- \(N_{Fr}\) Froude number \(\equiv \frac{V^2}{\infty \rho / r g (\rho-\rho_a)}\)
- \(N_{Kn}\) Knudsen number = \(\frac{\lambda}{a}\)
- \(N_{Nu}\) Nusselt number = \(2 f_h (2 \text{ times heat ventilation coefficient, c.f. } N_{Sh})\)
- \(N_{Pe}\) Peclet number \(\equiv 2 V_{\infty} r / D = N_{Sc} N_{Re}\)

(release strength of the particle diffusion and convective transport)

- \(N_{Pr}\) Prandtl number = \(\nu_a / \kappa_a\) (heat diffusion strength, c.f. \(N_{Sc}\))
- \(N_{pp}\) physical property number = \(\frac{\sigma_{w,a}^2}{\eta_{a}^4} g (\rho_w - \rho_a)\)
- \(N_{Re}\) Reynolds number \(\equiv 2 V_{\infty} r / \nu\)
\[ N_{Kn} \quad \text{Knudsen number} \equiv \frac{\lambda_{a}}{r_{p}} \]

\[ N_{S} \quad \text{Stokes number} = \frac{2 \tau_{2}^{2} \rho_{2} V_{x,1}}{9 \eta r_{1}} \left( \frac{24}{C_{D} N_{Re}} \right)^{1/2} \]

\[ N_{Sc} \quad \text{Schmidt number} \equiv \frac{v}{D} \quad \text{(mass diffusion strength, c.f. } N_{Pr}) \]

\[ N_{Sh} \quad \text{Sherwood number} = 2 f_{v} \quad \text{(2 times mass ventilation coefficient, c.f. } N_{Nu}) \]

zeroth moment of a distribution function

\[ P \quad \text{pressure} \quad \text{[Pa], [J m}^{-3}] \]

\[ P_{o} \quad \text{standard atmospheric pressure} = 101325. \]

probability function

\[ q \quad \text{bin-sizing factor} \]

\[ q \quad \text{mass fractions of condensed water:} \]

\[ q_{\text{liq}} \quad \text{mass fraction of total condensate that is liquid} \]

\[ q_{\text{rim}} \quad \text{mass fraction of total condensate that is rime ice} \]

\[ q_{\text{dep}} \quad \text{mass fraction of total condensate that is depositional ice} \]

\[ Q \quad \text{heat flux in the thermophoretic collection kernel} \quad \text{[J m}^{-2} \text{s}^{-1}] \]

\[ = \frac{k_{a}}{r_{w}(T_{a} - T_{w})} \]

\[ Q \quad \text{solubility} \quad \text{[mol mol}^{-1}] \]

\[ r \quad \text{radius} \quad \text{[m]} \]

\[ r_{d} \quad \text{drop radius} \]

\[ r_{w} \quad \text{drop radius} \]

\[ r_{i} \quad \text{ice particle spherical equivalent radius} \]

\[ r_{AS} \quad \text{dry size of ammonia sulfate particles} \]

\[ R \quad \text{specific gas constants:} \quad \text{[J Kg}^{-1} \text{K}^{-1}] \]

\[ R_{a} \quad \text{gas constant for dry air} = 287.04 \]

\[ R_{v} \quad \text{gas constant for water vapor} = 461.50 \]

\[ \mathcal{R} \quad \text{universal gas constant} = 8.3144 \quad \text{[J mol}^{-1} \text{K}^{-1}] \]

\[ s \quad \text{specific entropy} \quad \text{[J mol}^{-1} \text{K}^{-1}] \]

supersaturation ratios:
\[ s_{v,i} \text{ supersaturation ratio of water vapor over ice} = S_{v,i} - 1 \]
\[ s_{v,w} \text{ supersaturation ratio of water vapor over liquid water} = S_{v,w} - 1 \]

\[ S \text{ entropy} \quad [\text{J K}^{-1}] \]

saturation ratios:
\[ S_{v,i} \text{ saturation ratio of water vapor over ice} \]
\[ S_{v,w} \text{ saturation ratio of water vapor over water} \]

surface energies:
\[ S_T \text{ total surface energy of colliding drops} \]
\[ S_C \text{ surface energy of the coalesced drop} \]

\[ t \text{ time} \quad [\text{s}] \]

\[ T \text{ temperature} \quad [\text{K}] \]
\[ T_o \text{ absolute temperature of melting point} = 273.15 \]
\[ T_c \text{ temperature in °C} \quad [\text{°C}] \]

\[ U \text{ internal energy} \quad [\text{J}] \]

\[ v, V \text{ volume} \quad [\text{m}^3] \]

\[ V \text{ velocities:} \quad [\text{m s}^{-1}] \]
\[ V_\infty \text{ terminal velocity} \]
\[ V_{imp} \text{ impact velocity} \]

\[ W, W \text{ updraft velocity} \quad [\text{m s}^{-1}] \]

\[ W \text{ wet removal rate} \quad [\text{mol m}^{-3} \text{s}^{-1}] \]

mass flux in the diffusiophoretic collection kernel
\[
= \frac{D_v (\rho_{v,\infty} - \rho_{x,d})}{r_d M_w}
\]

\[ x \text{ bin variable} \]

\[ x \text{ molar mixing ratio in the liquid} \quad [\text{mol mol}^{-1}] \]

\[ y \text{ molar mixing ratio in air} \quad [\text{mol mol}^{-1}] \]

\[ Z \text{ moving averages in the Brown's quadratic exponential scheme} \]
\( \alpha \)  
Specific volume \([\text{m}^3 \text{ mol}^{-1}]\)

\[
\text{coefficient in the Cunningham slip-flow correction factor} = 1.257 + 0.4 \exp(-1.1/N_{Kn})
\]

\( \alpha_c \)  
Condensation coefficient

\( \beta^* \)  
Henry's law modification factors

\( \Delta \)  
Thickness of molecular transfer boundary layer \([\text{m}]\)

\( \varepsilon \)  
Eccentricity of an ellipse

\( \varepsilon \)  
Relative removal efficiency

\( \phi \)  
Axial ratio (aspect ratio) = \( c/a \)

\( \Phi \)  
Ratio of vapor density gradient at the basal faces to that at the prism faces

\( \gamma \)  
Lapse rates: \([\text{K} \text{ gpKm}^{-1}]\)

\[
\begin{align*}
\gamma_d & \quad \text{Dry lapse rate} = 9.76 \\
\gamma_m & \quad \text{Moist lapse rate} \\
\gamma_w & \quad \text{Water-saturation adiabatic lapse rate} (= 6.59 \text{ at } 0 \, ^\circ\text{C}, 1000 \text{ mb})
\end{align*}
\]

\( \Gamma \)  
Inherent growth ratio for the diffusional growth of ice particles

\( \eta \)  
Dynamic viscosity of air \([\text{Kg} \text{ m}^{-1} \text{ s}^{-1}]\)

\[
\begin{align*}
\eta & = \eta_o + 4.9 \times 10^{-8} T_c & \text{for } T \geq T_o \\
& = \eta_o + 4.9 \times 10^{-8} T_c - 1.2 \times 10^{-10} T_c^2 & \text{for } T < T_o
\end{align*}
\]

\( \eta_o \)  
Dynamic viscosity at 0 \( ^\circ\text{C} \) = 1.718 \( \times 10^{-5} \)

\( \Theta \)  
Specific sensible heat \([\text{J} \text{ mol}^{-1}]\)

\( \lambda \)  
Mean free path of air molecule = 6.62 \( \times 10^{-8} \) \( (P_o/P) \sqrt{T/T_o \ (\eta/\eta_o)} \) \([\text{m}]\)

\( \Lambda \)  
Slope of the Marshall-Palmer drop size distribution \([\text{m}^{-1}]\)
\( \mu \) chemical potential
constant surface in the spheroidal coordinate
mode of normal distribution

\( \nu \) kinematic viscosity of air = \( \eta / \rho_a \) \[m^2 \text{ s}^{-1}\]

\( \rho \) densities:
\[
\begin{align*}
\rho_a & \quad \text{density of air (}= 1.225 \text{ at STP)} \\
\rho_{\text{AS}} & \quad \text{density of ammonia-sulfate (}= 1769. \text{ at STP)} \\
\rho_i & \quad \text{bulk density of ice} = 916.7 - 0.175 T_c - 5 \times 10^{-4} T_c^2 \\
\rho_{\text{rime}} & \quad \text{rime density} \\
\rho_w & \quad \text{density of water} \\
& \quad = (999.84 + 18.225 T_c - 7.9222 \times 10^{-3} T_c^2 - 5.5448 \times 10^{-5} T_c^3 + \\
& \quad 1.4976 \times 10^{-7} T_c^4 - 3.9330 \times 10^{-10} T_c^5) / (1 + 0.018160 T_c) \\
& \quad 0 \leq T_c \leq 100 \text{ oC} , \ p = 1 \text{ atm} \\
& \quad = 999.84 + 0.0860 T_c - 0.0108 T_c^2 \\
& \quad -50 \leq T_c \leq 0 \text{ oC} , \ p = 1 \text{ atm} \\
\rho_s & \quad \text{saturation water vapor density} \\
\rho_v & \quad \text{water vapor density}
\end{align*}
\]

\( \sigma \) surface tensions (energies):
\[
\begin{align*}
\sigma_{i,a} & \quad \text{surface tension of ice against air} = \sigma_{i,w} + \sigma_{w,a} \\
\sigma_{w,a} & \quad \text{surface tension of water against air} = 0.0761 - 1.55 \times 10^{-4} T_c \\
\sigma_{i,w} & \quad \text{surface tension of ice against water} = 0.0285 + 2.5 \times 10^{-4} T_c \\
\sigma_{AB} & \quad \text{average molecular diameter in the Chapman-Enskog's binary diffusion theory} \ [\text{Å}]
\end{align*}
\]

\( \tau \) characteristic time, time constant \[\text{s}\]

\( \xi \) nonlinearity adjustment factor
decay rate coefficient in a first-order rate equaiton

\( \Omega_{AB}^{(1,1)} \) collision integral in the Chapman-Enskog's binary diffusion theory
Subscripts:

a  air

d  drop, dry air

g  gas-phase

h  heat

i  ice

l  aqueous-phase

p  particle

s  saturation

w  liquid water

∞  ambient environment, terminal velocity
Appendix B

CONFERENCE DISCUSSIONS ON THE MATERIAL IN SECTION 4.2

J. L. COLLETT. Your simulations reveal an absence of drops with diameters smaller than about 10 µm. This seems to be at odds with many field observations of continental clouds. What might account for the discrepancy?

J. P. CHEN. It could be caused by several mechanisms that were not considered in the model. First, turbulence in the cloud may bring drops of different growth history together. Also, small-scale turbulence causes drops in the same proximity to experience different updraft velocities. Such “turbulent-scale condensation” may diversify the growth process and broaden the drop distribution. As you pointed out in your next question, natural CCN composition is usually multi-component, which may play a role here. But I speculate that, as will be shown later, it is not an important factor.

J. L. COLLETT. What results would you expect from a multi-component aerosol? For example, assume that you have a mixture of small ammonium-sulfate and large sodium chloride particles.

J. P. CHEN. The CCN composition is not a direct factor for the condensation growth. Rather, the solute effect depends on the total number of ions that can be provided by each CCN particle. A 10^{-14} g (~0.1 µm) ammonium-sulfate particle is equivalent to a 2.2 \times 10^{-15} g (~0.06 µm) sodium-chloride particle in terms of their nucleation ability. So, I expect a similar result from either an internal or external mixture of multi-component CCN unless a very different CCN spectrum is used.

J. L. COLLETT. Thinking about your results from a different perspective, can you describe for us how the average solute concentration varies with drop size?
J. P. CHEN. The variation of the average solute concentration with drop size is shown by the heavy lines in the figure below (for the coalescence case). It varies over four orders of magnitude initially (1.5 hr). As time progresses, drops of different solute concentration gradually coalesce and result in large drops with concentrations approaching that of “bulk cloud water” (2.5 hr). Let me point out two things here: (1) the average concentration is time dependent; (2) although the variation of average concentration with size seems to be diminishing with time, large variations still exist within drops of the same sizes, as can be seen from the two extremes, indicated by the thin lines (shaded area is for 1.5 hr). So, caution must be made not to discuss only the mean concentrations. It is the variation that causes the deviation from bulk water chemistry.

Figure B1: The variation of the solute concentration with drop size (bin number). Heavy lines are the averages of drops with the same water bin number, and thin lines are the envelope of the variation. Shaded area is for 1.5 hr.
R. C. Easter. It would be most informative for the “bulk modeling” community if
you could show quantitatively the differences between your discretized model and
a bulk chemistry model for the same set of conditions. Have you made such
calculations?

J. P. Chen. Not yet. But I would certainly like to have it done in the near future.

G. A. Isaac. For your model, you used solute bins with “dry radii”. Why not use
water concentrations instead? This would seem to be the most chemically
significant parameter.

J. P. Chen. In our model setup, it is necessary to use a conservative property as a bin
component. That is why the solute mass was chosen instead of solute
concentration, which depends on both the water and solute mass. Also, it was
our intention to demonstrate the evolution of CCN spectrum (mass or size
distribution). But since solute concentration is probably a more common
parameter used in this science community, I put in the concentration isopleths in
Figure 1 as a remedy.

G. A. Isaac. The authors might comment on the importance of their modelled effects
on in-cloud chemical reactions. What errors would result if bulk chemistry is
assumed?

J. P. Chen. The model showed that there is a large variation of solute concentration
among drops from the mean (or “bulk”) concentration. Hegg and Larson (1990),
Ayers and Larson (1990), as well as Pandis and Seinfeld (1991, Sampling a size-
and composition-distributed droplet population, this Proceedings), have shown
that such variation may cause large deviations in the equilibrium and kinetic
chemistry from that in bulk water models. Bulk water chemistry tends to
underestimate the sorption of trace gases and in-cloud oxidation rates and lead to
errors in the scavenging of atmospheric trace chemicals. However, the
magnitudes of the errors are yet to be determined.
G. A. ISAAC.  The observational evidence for chemical dependence on droplet size is very limited to a few cases (Isaac and Daum 1987, A winter study of air, cloud and precipitation chemistry in Ontario, Canada, *Atmospheric Environment* **21**, 1587-1600;  Ogren et al., 1988, Measurement of the size-dependence of solute concentrations in cloud droplets, *Tellus* **41B**, 24-31) and restricted to condensational growth in the lowest layers (e.g. 300 m) of non-precipitating stratiform clouds.  Larger differences have been observed between bulk cloud water and precipitation from the same cloud systems.  The cloud water usually has higher solute concentrations.  Can the authors comment on this?

J. P. CHEN.  Since raindrops are just the mixture of many cloud drops in warm clouds, bulk rainwater should have similar solute concentrations to that in the bulk cloud water, provided that they were formed in the same air parcel.  But raindrops collected at the same level as the cloud drops are normally from higher levels due to sedimentation.  I can think of three possible causes for rain drops formed at a higher altitude to be less concentrated than cloud drops: (1) upper level air has fewer CCN per mole of air to share the condensed water;  (2) more water condensed out at lower temperatures, leading to further dilution;  (3) raindrops were originated from melted ice.

J. SLANINA.  I agree completely with your conclusion that this kind of modeling is necessary to understand scavenging processes.  It would be nice though, to see a validation of the model results using experimental data.  Have you done any validation of this kind?

J. P. CHEN.  No.  But I certainly would like to have such opportunity.
VITA

BIRTH DATE AND PLACE: August 11, 1959, Taipei, Taiwan, Republic of China

EDUCATION:
- National Taiwan University, June 1982, B.A. Atmospheric Sciences
- South Dakota School of Mines and Technology, December 1986, M.S. Meteorology.

PROFESSIONAL EXPERIENCE:
- 1/87→10/92 Research Assistant, Department of Meteorology, Penn State University
- 8/85→12/86 Research Assistant, Department of Meteorology, South Dakota School of Mines and Technology
- 9/84→7/85 Teaching Assistant, Department of Atmospheric Sciences, National Taiwan University
- 10/82→8/84 Weather Officer, 2nd Lt., Weather Wing, Chinese Air Force

PUBLICATIONS: