Parameterization of cloud droplet formation in global climate models

Athanasios Nenes and John H. Seinfeld
Department of Chemical Engineering, California Institute of Technology, Pasadena, California, USA

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An aerosol activation parameterization has been developed based on a generalized representation of aerosol size and composition within the framework of an ascending adiabatic parcel; this allows for parameterizing the activation of chemically complex aerosol with an arbitrary size distribution and mixing state. The new parameterization introduces the concept of “population splitting,” in which the cloud condensation nuclei (CCN) that form droplets are treated as two separate populations: those that have a size close to their critical diameter and those that do not. Explicit consideration of kinetic limitations on droplet growth is introduced. Our treatment of the activation process unravels much of its complexity. As a result of this, a substantial number of conditions of droplet formation can be treated completely free of empirical information or correlations; there are, however, some conditions of droplet activation for which an empirically derived correlation is utilized. Predictions of the parameterization are compared against extensive cloud parcel model simulations for a variety of aerosol activation conditions that cover a wide range of chemical variability and CCN concentrations. The parameterization tracks the parcel model simulations closely and robustly. The parameterization presented here is intended to allow for a comprehensive assessment of the aerosol indirect effect in general circulation models.

INDEX TERMS: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0320 Atmospheric Composition and Structure: Cloud physics and chemistry; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); KEYWORDS: aerosols, clouds, CCN, parameterization, indirect effect, GCM


1. Introduction

The most uncertain of all climate forcings is the aerosol indirect effect [Intergovernmental Panel on Climate Change, 2001]. There are two reasons for this. The first reason originates from the wide range of length scales involved in cloud-aerosol interactions: from hundreds of kilometers (that of the largest cloud systems) down to tens of meters (that of individual updrafts responsible for the production of new drops). Sizes of typical general circulation model (GCM) grid cells range from 4° × 5° to 2° × 2°. Such grid sizes can resolve only the largest cloud systems. To estimate how aerosol perturbations affect cloud properties from first principles, one needs to explicitly resolve processes that take place down to the smallest scales of new droplet formation. Cloud-resolving large eddy simulations can potentially address these smaller-length scales, but the computational burden associated with such simulations prohibits their use in climate models. The second reason lies in the sheer complexity of aerosol-cloud interactions themselves.

The first attempts to relate cloud properties to aerosols in GCMs [e.g., Boucher and Lohmann, 1995; Kiehl, 1999] empirically linked cloud droplet number concentration to a property available in a global aerosol model, such as total aerosol sulfate mass [e.g., Boucher and Lohmann, 1995] or total aerosol number [e.g., Gultepe and Isaac, 1996]. The empirical relationship itself is subject to substantial uncertainty; aerosol-cloud interactions are highly complex and cannot be represented by a simple correlation based on a single aerosol property. This is illustrated by the Kiehl et al. [2000] study, in which several different empirical relationships yield estimates of the global annual average indirect forcing ranging between −0.40 W m⁻² and −1.78 W m⁻². To address the deficiencies of purely empirical correlations, first-principle approaches to predicting cloud droplet number have emerged [e.g., Ghan et al., 1997; Lohmann et al., 1999].

The calculation of cloud droplet number from first principles entails setting up a cloud droplet number balance in each GCM grid cell:

\[ \frac{dN_d}{dt} = Q_{\text{activation}} - Q_{\text{evaporation}} - Q_{\text{collision}} + Q_{\text{advection}} + \ldots, \] (1)
where \( N_D \) is the droplet number concentration, \( Q_{\text{activation}} \) is the droplet source from droplet activation, \( Q_{\text{evaporation}} \) is the loss from droplet evaporation, \( Q_{\text{collision}} \) is the loss from collision-coalescence processes, and \( Q_{\text{detection}} \) is the net source of droplets advected from adjacent grid cells (other processes can be present, particularly if the cloud contains ice or is precipitating). Cloud droplet activation is a key process for the indirect effect since it is the direct microphysical aerosol-cloud link. Explicitly resolving each of these processes from first principles necessitates resolution on scales of tens of meters since this is the smallest scale for which aerosol droplet activation, and hence cloud formation, can take place. Such resolutions are far beyond anything computationally feasible for GCMs. As a consequence, a prognostic GCM estimate of the aerosol indirect effect must rely on parameterizations of all such subgrid processes. The implementation of explicit aerosol activation within a GCM presupposes that the dynamics of cloud formation (particularly the probability distribution of updraft velocity or of cooling rate below cloud) and the aerosol characteristics below cloud are known. Such dynamical information is not readily available from a GCM, so it must be obtained from a parameterization. The basic theory of aerosol activation is well established, and many numerical models describing it have appeared in the literature [e.g., Jensen and Charlson, 1984; Flossmann et al., 1985; Pruppacher and Klett, 1997; Seinfeld and Pandis, 1998; Nenes et al., 2001]: the inclusion of numerical activation models is in itself computationally challenging, so the activation process needs to be parameterized. Parameterization of the subgrid cloud dynamics is not addressed in the current study.

In parameterizations of aerosol activation that have appeared in the literature over the years, treatments of the aerosol size distribution and the activation process differ. The first parameterization appeared 4 decades ago [e.g., Twomey, 1959; Squires and Twomey, 1960]. Although providing elegant solutions and simple expressions for the number of nucleated droplets, these approaches rely on both simple aerosol size distributions (power law) and idealized expressions for the droplet condensation rate. As a result, systematic errors arise in their predictions, such as a prediction of droplet number that exceeds the total condensation nuclei. Other subsequent approaches have adopted a functional relationship between the number of cloud condensation nuclei (CCN) that activate at a given supersaturation level (otherwise known as the “CCN spectrum”). Feingold and Heymsfield [1992] adopted a power law to describe the CCN spectrum, although their approach can be extended to any functional form. Cohard et al. [1998, 2000], in their treatment, assumed a generalized sigmoidal functional form. The abstraction and detachment from assumptions regarding size distribution and chemical homogeneity can theoretically allow any size distribution to be described through the generalized CCN spectrum. Other parameterizations have used lognormal representations of aerosol size distributions and have used Köhler theory to compute the CCN spectrum [e.g., Ghan et al., 1993, 1995; Abdul-Razzak et al., 1998; Abdul-Razzak and Ghan, 2000]. Abdul-Razzak and Ghan [2002] propose an algorithm for the use of their multiple lognormal population parameterization [Abdul-Razzak and Ghan, 2000] in sectional aerosol models. Their approach is to use an empirically prescribed value of geometric dispersion and to treat each section as a separate mode. Chuang and Penner [1995] parameterized sulfate transfer to and production in preexisting particles by condensation of gas-phase sulfuric acid and aqueous oxidation of sulfur dioxide. The most sophisticated current aerosol activation parameterizations still rely principally on empirical information obtained from detailed numerical parcel simulations. To compute the number of activated droplets, Feingold and Heymsfield [1992] compute the cloud maximum supersaturation from a nonlinear equation which contains a parameter evaluated through multivariate regression of numerical adiabatic parcel calculations. Abdul-Razzak et al. [1998] and Abdul-Razzak and Ghan [2000] calculate the maximum parcel supersaturation explicitly by using a correlation derived from the regression of numerical parcel calculations. Khvorostyanov and Curry [1999] assume a power law aerosol size distribution to develop an analytical expression linking CCN number concentration to parameters that are related to aerosol growth under subsaturated conditions. [c] To summarize, previous aerosol activation parameterizations assume one (or more) of the following: (1) specified aerosol size distributions (power law, lognormal) or a prescribed activation spectrum; (2) uniform chemical composition over particle size composed of only a completely soluble and insoluble fraction; (3) a single aerosol population (that is, an internally mixed aerosol); and (4) “instantaneous” activation of CCN (absence of kinetic effects). Any of these assumptions, under certain conditions, may not be satisfied, so an application of the parameterization may lead to bias. The aerosol may be chemically complex; its composition can vary considerably with size and may be externally mixed. Certain aerosol chemical components can alter the activation behavior in a manner which is not easily introduced in parameterizations. For example, the presence of surface-active species such as those that tend to lower the droplet surface tension facilitate the activation of CCN [Facchini et al., 1999]. The amount of surface tension depression depends on the concentration of the dissolved organic [e.g., Shulman et al., 1996; Charlson et al., 2001]; since the concentration of dissolved species at the point of activation varies considerably with CCN dry size, one cannot assume a uniform or average change in surface tension throughout the CCN population. The resulting modified Köhler equation for such CCN cannot be solved explicitly for their critical supersaturation, \( s_c \). As most extant parameterizations rely on an explicit link between \( s_c \) and dry CCN diameter, it is difficult to incorporate the implicit link surface-active species impose between \( s_c \) (or \( D_c \)) and the CCN dry size. Similar difficulties arise from the presence of slightly soluble species [Laaksonen et al., 1998], which can also exhibit surface-active behavior. Such “chemical” effects cannot be neglected, as they can potentially constitute a large component of the aerosol indirect effect [Charlson et al., 2001; Nenes et al., 2002a]. Also, with the emergence of global aerosol models that allow completely general distributions of both size and composition [Adams and Seinfeld, 2002] the stipulation of a prescribed distribution may be overly constraining. For example, the constraint that the aerosol has to follow a lognormal distribution has been shown to lead to discrepancies in droplet number when applied in a one-dimensional
climate model [Zhang et al., 2002]. The generalized CCN spectrum approach of Cohard et al. [1998, 2000], when used in conjunction with a GCM simulation of global aerosols, necessitates an undesirable on-line curve-fitting procedure.

[7] Although utilizing empirical information can be a powerful tool, it is desirable, for the sake of generality and robustness, to minimize the amount of such information contained within a parameterization. It is not clear when a parameterization, which is based on empirical fits, will exhibit biases in the prediction. For example, Abdul-Razzak and Ghan [2002] show that the sectional version of their activation parameterization follows a full numerical activation model for high updraft velocities, but the performance deteriorates as the updraft velocity decreases. For lognormal aerosol the parcel model results are generally reproduced well when 10–90% of the aerosol becomes activated [Abdul-Razzak and Ghan, 2000; Abdul-Razzak et al., 1998].

[8] The present work develops a new aerosol activation parameterization, intended for use in GCMs, which is based on a generalized representation of aerosol size and composition within the framework of an adiabatic cloud parcel. Explicit treatment of mass transfer (kinetic) limitations in droplet growth is included. We focus on minimizing the amount of empirical information included within the parameterization. In the sections that follow we present the derivation of the activation parameterization and then outline its use. We compare the new parameterization with that of Abdul-Razzak and Ghan [2000]; the two are compared to the predictions of a cloud parcel model with detailed growth kinetics for a variety of CCN activation conditions.

2. Definition of Size Distributions

[9] Although any size distribution (such as a power law or lognormal) can be used in the new parameterization, we select a sectional representation to allow the most general possible representation of aerosol size and composition. In this representation we divide the aerosol into an arbitrary number of size sections, each of which has its own chemical composition. Each section, \( m \), is characterized by its lower and upper diameters, \( D_{p,m-1} \) and \( D_{p,m} \) respectively, and by the total number concentration of particles in the section, \( N_m \) (Figure 1a). The aerosol chemical composition within each section is assumed to be uniform and independent of those in other sections. A linear profile (which is a common assumption for sectional implementations of aerosol microphysics) of aerosol number concentration across a section is assumed. With these assumptions the size distribution, \( n^D(D_p) = dN/dD_p \) over \( D_{p,m-1} \leq D_p < D_{p,m} \), is given by

\[
n^D(D_p) = \frac{dN}{dD_p} = \frac{N_m}{D_{p,m} - D_{p,m-1}},
\]

and the cumulative size distribution (total number of particles with a diameter smaller than \( D_p \)), \( F^D(D_p) \), is given by

\[
F^D(D_p) = \int_0^{D_p} n^D(D'_p) dD'_p = \sum_{j=1}^{m-1} N_j + N_m \left( \frac{D_p - D_{p,m-1}}{D_{p,m} - D_{p,m-1}} \right),
\]

where \( m \) is the section that contains \( D_p \).

Figure 1. Illustration of the sectional representation of (a) aerosol number distribution, \( n^D(D_p) \), and (b) supersaturation distribution, \( n^S(s) \).

[10] The above treatment assumes a single aerosol population. Multiple aerosol populations can exist (externally mixed aerosol); in this case a separate size distribution, \( n^D_k(D_p) \), is defined for each population \( k \). Then the cumulative size distribution is given by summing over all the populations:

\[
F^D(D_p) = \sum_{k=1}^{k} \int_0^{D_p} n^D_k(D'_p) dD'_p = \sum_{l=1}^{k} \sum_{j=1}^{m(l)-1} N_{j,l} + \sum_{j=1}^{m(l)} N_{j,l} \left( \frac{D_p - D'_{p,m(l)-1}}{D_{p,m(l)} - D'_{p,m(l)-1}} \right),
\]

where \( D'_{p,m(l)-1} \) and \( D_{p,m(l)} \) are the boundaries of section \( l \) that contain \( D_p \) and population \( l \). The variable \( m(l) \) is used to indicate that each population \( l \) has its own section boundaries.

3. Definition of CCN Spectrum

[11] After the size distributions are defined for each of the aerosol populations, \( n^D(D_p) \) is then mapped to supersatura-
tion space (Figure 1b) and the critical supersaturation distribution, \( n'(s) \), is obtained:

\[
n'(s) = \frac{dN}{ds} = \frac{N_i}{s_{c,i} - s_{c,i-1}}, \quad s_{c,i-1} \leq s < s_{c,i}
\]

where \( s_{c,i-1} \) and \( s_{c,i} \) are the critical supersaturations corresponding to the boundaries of section \( i \). For simplicity we assumed that \( n'(s) \) is piecewise linear. We change the index used for representing a section from \( m \) to \( i \) to reflect the change in the ordering of the sections as they are mapped onto (monotonically increasing) supersaturation space.

[12] The critical supersaturation corresponding to the section boundaries can be calculated using Köhler theory; that is, the critical supersaturation corresponding to the diameter of each section boundary is calculated. We will not present a procedure for calculating the critical supersaturation of the sectional boundaries, as it is a standard procedure that can be found throughout the literature [e.g., Seinfeld and Pandis, 1998]. We would like to note, however, that we do not need an explicit link between aerosol dry size and critical supersaturation, a restraint which is necessary in most parameterizations. Relaxing this restraint allows for addressing the activation of highly complex activation curves, such as those seen for slightly soluble and surface-active compounds [Shulman et al., 1996].

[13] The sectional representation of the CCN spectrum (total number of particles with critical supersaturation smaller than \( s \) ), \( F^i(s) \), is given by

\[
F^i(s) = \int_0^s n'(s')ds' = \sum_{j=1}^{i-1} N_j + N_i \left( \frac{s - s_{c,i-1}}{s_{c,i} - s_{c,i-1}} \right),
\]

where \( i \) is the section that contains \( s \) and where \( s_{c,0} = 0 \).

[14] When \( k \) populations exist, the CCN spectrum is obtained by summing over all the aerosol populations:

\[
F^i(s) = \sum_{j=1}^{k} \left( \int_0^s n^i_j(s')ds' \right) = \sum_{j=1}^{k} \left( \sum_{l=1}^{i-1} N_{il,j} + N_{i,j} \left( \frac{s - s_{c,i(l)-1}}{s_{c,i(l)} - s_{c,i(l)-1}} \right) \right),
\]

where \( s_{c,i(l)-1} \) and \( s_{c,i(l)} \) are the critical supersaturations for the boundaries of section \( i \) and population \( l \) that bound \( s \). The variable \( i(l) \) is used to indicate that each population \( l \) has its own section boundaries.

[15] Equation (7) represents the CCN spectrum of the aerosol; once the maximum parcel supersaturation, \( s_{\text{max}} \), is known, the number of CCN that will activate into drops, \( N_d \), is given by

\[
N_d = F^i(s_{\text{max}}).
\]

4. Formulation of the Aerosol Activation Parameterization

[16] The aerosol activation parameterization is developed in two steps. The first step involves the representation of the aerosol number and the chemical composition distribution with respect to size and the calculation of the number concentration of droplets that can potentially form at a certain level of supersaturation (the CCN spectrum). Modified Köhler theory, which embodies effects of surfactant and slightly soluble species, is used to compute the supersaturation needed for a CCN to activate [Shulman et al., 1996; Laaksonen et al., 1998]. In the second step the CCN spectrum is included within the framework of an adiabatic cloud parcel model, with a specified updraft velocity (or cooling rate), to compute the maximum supersaturation, \( s_{\text{max}} \), of the cloud parcel. The number concentration of nucleated drops is calculated from equation (8).

[17] Considerable attention has been given to the approximation used in estimating the droplet size at the point of parcel maximum supersaturation (which is a key parameter, as it controls the condensation rate). A common assumption made is that the CCN grows instantaneously to its critical diameter when the parcel supersaturation becomes equal to the CCN’s critical supersaturation; that is, the activation process is not kinetically limited. When this condition is not satisfied, it can be a source of significant error in the prediction of the number of activated droplets [Nenes et al., 2001]; this is one of the issues addressed in the new parameterization. We would like to note that the previously described kinetic limitation mechanism has long been known [e.g., Jensen and Charlson, 1984; Chuang et al., 1997]; this was called “inertial” kinetic limitation by Nenes et al. [2001]. In addition to the “inertial” mechanism, Nenes et al. [2001] also identified two other kinetic limitation mechanisms, the “deactivation” and “evaporation” mechanisms. In this study, we only consider the “inertial” mechanism, as it can have a substantial effect on the condensation rate and thus on \( s_{\text{max}} \).

4.1. Computation of Parcel Maximum Supersaturation

[18] In an adiabatic parcel the rate of change of the supersaturation, \( s \), for a cloud parcel that ascends with a constant vertical velocity, \( V \), is [Pruppacher and Klett, 1997; Seinfeld and Pandis, 1998]

\[
\frac{ds}{dt} = \alpha V - \gamma \frac{dW}{dt},
\]

where

\[
\alpha = \frac{gM_w \Delta H_w}{c_p RT^2}, \quad \gamma = \frac{p M_w - M_o \Delta H_w^2}{c_p RT^2},
\]

and where \( \Delta H_w \) is the latent heat of condensation of water, \( T \) is the parcel temperature, \( M_w \) is the molecular weight of water, \( g \) is the acceleration of gravity, \( M_o \) is the molecular weight of air, \( c_p \) is the heat capacity of air, \( p^* \) is the water saturation vapor pressure, \( p \) is the ambient pressure, \( dW/dt \) is the rate of condensation of liquid water onto the drops, and \( R \) is the universal gas constant. The first term on the right hand side of equation (9) expresses the tendency of supersaturation to increase from the cooling of the parcel, while the second term expresses the tendency of supersaturation to decrease because of depletion of water vapor by the activated droplets.
The rate of water condensation on the droplet population can be expressed as
\[
\frac{dW}{dt} = \frac{\pi}{2} \rho_w \int_0^s D_p \cdot \frac{dP}{dt} n'(s') ds'.
\]  \(11\)
where \(\rho_w\) is the density of water. By substituting equation (11) into equation (9), we obtain
\[
\frac{ds}{dt} = \alpha V - \gamma \frac{\pi}{2} \rho_w \int_0^s D_p \cdot \frac{dP}{dt} n'(s') ds'.
\]  \(12\)
The parcel supersaturation reaches a maximum when water vapor availability from parcel cooling becomes equal to the depletion rate from the activated drops; this is expressed by setting \(ds/dt\) in equation (12) equal to zero:
\[
\alpha V - \gamma \frac{\pi}{2} \rho_w \int_0^{s_{\text{max}}} D_p \cdot \frac{dP}{dt} n'(s') ds' = 0.
\]  \(13\)
The rate of growth of a drop of diameter \(D_p\) is determined from [Seinfeld and Pandis, 1998]
\[
\frac{dD_p}{dt} = G \left(s - s_{\text{eq}}\right);
\]  \(14\)
where \(k_0\) is the thermal conductivity of air, \(D_t\) is the water vapor diffusivity, and \(s_{\text{eq}}\) is the equilibrium supersaturation of the droplet.
With the assumption that beyond the point of activation the growth rates are not significantly influenced by droplet curvature and solute effects, \(s_{\text{eq}} = 0\), equation (14) becomes [Twomey, 1959]
\[
\frac{dD_p}{dt} = G \cdot s.
\]  \(15\)
One can integrate equation (16) from time \(\tau\), when the parcel supersaturation is equal to the CCN critical supersaturation, to the time of maximum supersaturation, \(t_{\text{max}}\), to give the droplet diameter at the time of \(s_{\text{max}}\):
\[
D_p^* = D_p(\tau) + 2 \int_{\tau}^{t_{\text{max}}} G s dt.
\]  \(17\)
By substituting equations (17) and (16) into equation (13), we obtain
\[
2\alpha V - G s_{\text{max}} - \int_0^{s_{\text{max}}} \left(D_p^*(\tau) + 2G \int_{\tau}^{t_{\text{max}}} s dt\right) n'(s') ds' = 0.
\]  \(18\)
\[\text{Before proceeding further we need to evaluate the integral in equation (18), referred to hereafter as } I(0, s_{\text{max}}):
\]
\[
I(0, s_{\text{max}}) = G s_{\text{max}} \int_0^{s_{\text{max}}} \left(D_p^*(\tau) + 2G \int_{\tau}^{t_{\text{max}}} s dt\right) n'(s') ds'.
\]  \(19\)
where the parameters in the parentheses indicate the limits of integration. If \(I(0, s_{\text{max}})\) is evaluated and substituted into equation (18), the parcel maximum supersaturation can then be calculated, and a subsequent substitution into equation (8) would yield the cloud droplet number concentration.

### 4.2. Calculation of Integral \(I\)

An analytical expression for \(I\) is not possible, but \(I\) has two asymptotic limits. The first limit, \(I_1\), is obtained when
\[
D_p^2(\tau) \ll 2G \int_{\tau}^{t_{\text{max}}} s dt.
\]  \(20\)
In this limit the CCN experience significant growth beyond the point where they are exposed to \(s > s_c\). Note that the above approximation is used to derive the parameterization of Twomey [1959]. The supersaturation integral in equation (19) can be evaluated using the lower bound of Twomey [1959]:
\[
\int_{\tau}^{t_{\text{max}}} s dt \approx \frac{1}{2\alpha V} \left(s_{\text{max}}^2 - s(\tau)^2\right).
\]  \(21\)
where \(s(\tau)\) is the parcel supersaturation at time \(\tau\). Substituting equations (20), (21), and (5) into equation (19), we eventually obtain
\[
I_1(0, s_{\text{max}}) = \frac{s_{\text{max}} G^{3/2}}{(2\alpha V)^{3/2}} \sum_{j=1}^{i} \frac{N_j}{s_i^2 - s_{i-1}^2} \left[\frac{x}{2} \left(s_{2i}^2 - x^2\right)^{1/2} + \frac{s_{\text{max}}^2}{2} \cdot \arcsin \frac{x}{s_{\text{max}}} \right]_{x=s_j}^{x=s_{2i}},
\]  \(22\)
where the bracket signifies the difference between evaluation at \(x = s_j^2\) and \(x = s_{2i}^2\) and \(i\) is the section that contains \(s_{\text{max}}\) (i.e., \(s_{i-1}^2 \leq s_{\text{max}} \leq s_i^2\)).

The second limit, \(I_2\), of \(I\) is obtained when
\[
D_p^2(\tau) \gg 2G \int_{\tau}^{t_{\text{max}}} s dt,
\]  \(23\)
which physically means that the CCN do not experience significant growth beyond the point where they are exposed to \(s > s_c\). A common assumption (used in the parameterization of Ghan et al. [1993]) is that \(D_p(\tau)\) is equal to the critical diameter, \(D_c = 2A/3s_c\), when the parcel \(s\) becomes equal to the particle \(s_c\), \((A = 4M_w/\sigma RT \rho_w)\), and \(\sigma\) is the droplet surface tension at its critical diameter. This can be assumed when the timescale of particle growth is small compared to the rate at which supersaturation changes in the parcel [Chuang et al., 1997]; this implies that the CCN is in equilibrium with the parcel supersaturation until the point of activation and hence will instantaneously grow to \(D_c\) when exposed to its critical supersaturation. (We will elaborate on the implications of this
assumption in section 4.4.) Substitution of equation (23) into equation (19) (with the assumption that \( D_p(\tau) = D_c \)) and evaluation of the integral yields

\[
I_2(s_i^c, s_{\text{max}}) = \frac{2Gs_{\text{max}}}{3} \left[ \sum_{j=2}^{i-1} \left( \frac{N_j A_j}{s_j^c - s_i^c} \right) \ln \frac{s_j^c}{s_i^c} + \left( \frac{N_i A_i}{s_i^c - s_i^c} \right) \ln \frac{s_{\text{max}}}{s_i^c} \right],
\]

(24)

where \( A_j \) is an average \( A \) over section \( j \). Note that \( j \) starts from 2, otherwise \( I_2 \rightarrow \infty \) as \( s_i^c \rightarrow 0 \). This asymptotic limit will not be a problem for the parameterization, as \( I_2 \) will always be used with a nonzero lower bound. In equation (24), \( i \) is the section that contains \( s_{\text{max}} \) (i.e., \( s_{i-1}^c \leq s_{\text{max}} \leq s_i^c \)).

### 4.3. Concept of “Population Splitting”

[28] While neither of equations (22) or (24) alone are expected to describe the behavior of all the CCN during their activation, it is reasonable to divide the CCN into two groups: those that would follow equation (22) and others that would follow equation (24). This classification of CCN, which we call “population splitting,” will be used to approximate \( I \):

\[
I = I_1(0, s_{\text{part}}) + I_2(s_{\text{part}}, s_{\text{max}}).
\]

(25)

[29] The ordering of the two integrals is deliberate: \( I_1 \) is used for low \( s_c \) CCN, while \( I_2 \) is used for the remaining CCN. This ordering will be justified subsequently (in section 4.4). The upper bound of \( I_1 \) and the lower bound of \( I_2 \) in equation (25) is termed the “partitioning critical supersaturation,” \( s_{\text{part}} \) (Figure 2). Physically, this supersaturation defines two populations of droplets: one for which \( D_p \approx D_c \) and one for which either \( D_p \gg D_c \) or \( D_p \ll D_c \) (but still large enough to be considered a droplet). Note that equation (25) assumes that for a given population, there is only one \( s_{\text{part}} \). If \( s_{\text{part}} \) is known, the integral \( I \) can be evaluated and substituted into equation (18); \( s_{\text{max}} \) and \( N_d \)

\[
\text{can then be calculated. The procedure used for calculating}
\]

\[
s_{\text{part}} \text{ is developed in section 4.4.}
\]

### 4.4. Implementation of Population Splitting

[30] Numerical simulations with a cloud parcel model [Nenes et al., 2001] reveal that \( s_{\text{part}} \) depends on \( s_{\text{max}}, V \) and the CCN spectrum characteristics. We will now attempt to derive theoretical expressions for \( s_{\text{part}} \). An obvious candidate for \( s_{\text{part}} \) is the critical supersaturation of the CCN population, for which \( D_p(\tau) = 2G \int_{s_{\text{max}}}^{s_{\text{part}}} \text{d}t \). From equation (21) and substituting \( D_p(\tau) = 2A/3s_{\text{part}} \), we obtain

\[
\frac{4A^2}{9s_{\text{part}}^4} = G\left( s_{\text{max}}^2 - s_{\text{part}}^2 \right).
\]

(26)

where \( A = 4M_a\sigma_p/RT \) and \( \sigma_w \) is the surface tension of water. After some algebra, equation (26) leads to the quartic equation

\[
p(s_{\text{part}}) = s_{\text{part}}^4 - s_{\text{max}}^2 s_{\text{part}}^2 + 4A^2\sigma_pV/9G = 0.
\]

(27)

[31] If the discriminant, \( \Delta = s_{\text{max}}^4 - 16A^2\sigma_pV/9G \), of \( p(s_{\text{part}}) \) is nonnegative, then equation (27) has two real roots with respect to \( s_{\text{part}} ^{\prime} \):

\[
\begin{align*}
\left( \frac{s_{\text{part}}^{\prime}}{s_{\text{max}}} \right)^2 & = \frac{1}{2} \left[ 1 - \left( 1 - \frac{16A^2\sigma_pV}{9\pi^4 G} \right)^{1/2} \right], \\
\left( \frac{s_{\text{part}}^{\prime}}{s_{\text{max}}} \right)^2 & = \frac{1}{2} \left[ 1 + \left( 1 - \frac{16A^2\sigma_pV}{9\pi^4 G} \right)^{1/2} \right].
\end{align*}
\]

(28)

[32] Each of the two roots, \( s_{\text{part1,2}} \), expresses the \( s_c \) of those CCN for which their subsequent growth beyond activation is equal to \( D_c \). These two characteristic \( s_c \) divide the CCN population into three groups: those with \( s_c < s_{\text{part1,2}} \), those with \( s_{\text{part1,2}} < s_c < s_{\text{part1,3}} \), and those with \( s_{\text{part2,3}} < s_c \). If a CCN has an \( s_c \) between \( s_{\text{part1,2}} \) and \( s_{\text{part2,3}} \), then \( p(s_c) > 0 \), which means that the CCN experiences significant growth after it attains its critical diameter. For other values of \( s_c \), \( p(s_c) > 0 \), which means that the growth experienced by the CCN is smaller than its critical diameter. Note that the latter does not mean that when \( p(s_c) > 0 \), the CCN size can be approximated by its critical size; further knowledge of droplet growth kinetics is needed for deciding whether this approximation can be used.

[33] Of all the CCN that form droplets, those with the highest \( s_c \) have sizes close to their \( D_c \). This is because (1) high-\( s_c \) CCN are less influenced by kinetic limitations and thus would be in equilibrium with parcel supersaturation until the point of activation and (2) because they have the least time to grow beyond activation [Nenes et al., 2001]. This condition is valid for particles for which \( s_c > s_{\text{part2,3}} \). However, as \( s_c \) decreases, the time available for growth increases, and at some point the droplet growth becomes large enough to substantially exceed the CCN critical diameter. This happens for the particles for which \( s_{\text{part1,2}} < s_c < s_{\text{part2,3}} \). Apart from having the benefit of increased exposure time, a decrease in \( s_c \) also leads to a larger \( D_c \); at the value of \( s_c = s_{\text{part1,2}} \) the subsequent growth beyond activation becomes equal to \( D_c \); for lower \( s_c \), \( D_c \) is larger.
than the growth experienced by the particle. Therefore CCN for which \( s_c < s_{\text{part},1} \) are kinetically limited and do not attain their critical diameter. Equation (20) cannot be used to estimate the CCN size, as it never approaches its critical diameter (this is confirmed from simulations with a detailed adiabatic cloud model [Nenes et al., 2001]). Therefore approximating \( I \) with \( I_2 \) for the kinetically limited CCN can lead to large biases because their droplet size would be systematically overestimated by assuming \( D(\tau) = D_c \).

[34] Since those CCN, the growth of which is kinetically limited, have a small \( s_c \), it is reasonable to approximate their driving force for droplet growth (equation (14)), \( s - s_{eq} \) with \( s_c \) even before they activate (this is because \( s_{eq} \approx 0 \)). The growth of such a particle can then be expressed as

\[
D_c^2 \approx 2G \int_{\tau}^{t_{\text{max}}} s \, dt,
\]

which is equivalent to equation (20). Thus \( I_1 \) is used to approximate \( I \) for CCN with \( s_c < s_{\text{part},1} \). On this basis, \( s_{\text{part}} = s_{\text{part},2} \), and the following can be said:

\[
\begin{aligned}
\frac{s_c}{s_{\text{max}}} & \leq \frac{s_{\text{part}}}{s_{\text{max}}} \Rightarrow D_c^2(\tau) \leq 2G \int_{\tau}^{t_{\text{max}}} s \, dt \Rightarrow I \approx I_1; \\
\frac{s_c}{s_{\text{max}}} & > \frac{s_{\text{part}}}{s_{\text{max}}} \Rightarrow D_c^2(\tau) > 2G \int_{\tau}^{t_{\text{max}}} s \, dt \Rightarrow I \approx I_2.
\end{aligned}
\]

[35] The discriminant \( \Delta \) expresses the extent of kinetic limitations throughout the droplet formation and depends on \( s_{\text{max}} \) (which depends primarily on \( V \) and on CCN characteristics), \( V \), and the timescale of water vapor diffusion (embodied in \( G \)). \( \Delta = 0 \) marks a boundary between two growth regimes: one where most CCN are free from kinetic limitations (\( \Delta > 0 \)) and one in which kinetic limitations are dominant (\( \Delta < 0 \)). As \( \Delta \) increases, \( s_{\text{part},1} \to 0 \) and \( s_{\text{part},2} \to s_{\text{max}} \) so that more of the CCN attain sizes larger than their critical diameter; this means that fewer CCN are subject to kinetic limitation. (This is consistent with the analysis of Nenes et al. [2001], as increasing parcel \( s_{\text{max}} \) and \( V \) leads to rapid particle growth and therefore to a decrease in kinetic limitations.) The rules in equation (30) indicate that for a nonnegative \( \Delta \), \( (s_{\text{part}}/s_{\text{max}}) \geq \sqrt{0.5} \). In this regime, \( s_{\text{part}} \) decreases with decreasing \( s_{\text{max}} \).

[36] When \( \Delta < 0 \), equation (27) is without real roots; under these conditions, kinetic limitations in droplet growth are strong throughout the entire CCN population. Of all the CCN, those with the highest \( s_c \) would tend to have size of order \( D_c \) since (1) the timescale of activation decreases with particle size (or with increasing \( s_c \)) [Chuang et al., 1997] and (2) \( p(s_c) \) is closest to zero when \( s_c \to s_{\text{max}} \). Therefore for CCN of high \( s_c \), \( I_2 \) can be used to approximate \( I \). The lower \( s_c \) particles can be considerably smaller than their critical size, but with small \( s_c \), their growth, as before, can be represented by equation (29); \( I_1 \) will therefore be used to approximate \( I \). Consequently, equations (30) will still be used to approximate \( I \), even if \( \Delta < 0 \). On the basis of the previous discussion we anticipate that fewer CCN can attain their critical diameter as the parcel maximum supersaturation decreases; numerical simulations support this expectation. \( s_{\text{part}} \) increases with decreasing \( s_{\text{max}} \) and is calculated from

\[
\begin{align*}
\frac{s_{\text{part}}}{s_{\text{max}}} & = \min(0.666 \times 10^7 A_{\text{max}}^{-0.3824}, 1.0) = 1.0, \\
\text{Figure 3. } s_{\text{part}}/s_{\text{max}} \text{ as a function of } s_{\text{max}}. \text{ Each curve corresponds to a constant updraft velocity.}
\end{align*}
\]

the following correlation, derived from the regression of a large set of empirical \( s_{\text{part}} \) that reproduce the predictions of a detailed microphysics model:

\[
s_{\text{max}} = \min(0.666 \times 10^7 A_{\text{max}}^{-0.3824}, 1.0).
\]

[37] The simulations on which equation (31) is based were chosen so that \( \Delta < 0 \). In generating numerical values for equation (31) the mass accommodation coefficient of water vapor on aqueous drops is equal to 1.0 and \( T = 283 \) K. Equation (31) indicates that as \( s_{\text{max}} \to 0 \), \( s_{\text{part}}/s_{\text{max}} \to 1 \), meaning that as the \( s_{\text{max}} \) decreases, fewer and fewer of the CCN can attain their critical diameter. All the rest are kinetically limited.

[38] Combination of the two expressions for calculating \( s_{\text{part}} \) (equation (31) for \( \Delta < 0 \) and \( s_{\text{part}} = s_{\text{part},2} \) for \( \Delta > 0 \)) displays physically expected behavior. Figure 3 shows \( s_{\text{part}}/s_{\text{max}} \) as a function of \( s_{\text{max}} \). Each line corresponds to a different value of updraft velocity \( V \). Given that each curve in Figure 3 is for constant updraft velocity \( V \), \( s_{\text{max}} \) varies only because of changes in the aerosol concentration; Figure 3 thus displays the Twomey effect on \( s_{\text{part}} \). Note that there are regions for which \( s_{\text{part}} \) is insensitive to changes in \( s_{\text{max}} \); we would expect that simple parameterizations perform well in these regions, as they do not exhibit explicit dependence on \( s_{\text{max}} \). At large values of \( s_{\text{max}}, s_{\text{part}}/s_{\text{max}} \to 1 \), indicating that the vast majority of the CCN are not subject to kinetic limitations. For lower values of \( s_{\text{max}}, s_{\text{part}}/s_{\text{max}} \) reaches a minimum; a further decrease in \( s_{\text{max}} \), however, reverses the trend for \( s_{\text{part}}/s_{\text{max}} \), as explained above. An activation parameterization is severely tested in regions where \( s_{\text{part}} \) changes rapidly.

[39] It is also important to examine the behavior of \( s_{\text{part}} \) for constant aerosol concentration and variable updraft velocity. To do so, we need information regarding the relationship between aerosol concentration, \( V \), and \( s_{\text{max}} \). This is accomplished by using a numerical parcel activation model for the four aerosol types shown in Table 2. The
Figure 4. $s_{part}$/$s_{max}$ as a function of updraft velocity. Each curve corresponds to one of the aerosol types in Table 2. $s_{max}$ is computed using the numerical parcel model of Nenes et al. [2001].

results are shown in Figure 4. Clearly, we can see that for 
marine-type aerosols, $s_{part}$ is close to unity (meaning that the 
vast majority of the droplets attain sizes larger than their 
critical diameter) for all updraft velocities; the other extreme 
is the urban aerosol, which always experiences significant 
kinetic limitations. For the distribution used here, between 
20% and 40% of the particles do not reach critical size at 
any updraft velocity. These percentages agree well with 
the numerical results of Nenes et al. [2001] for the same aerosol 
size distributions; this is verification that the procedure used 
for calculating $s_{part}$ is realistic. (Note that the correlation was 
derived from many simulations.)

4.5. Final Form of Aerosol Activation Parameterization

[40] After the evaluation of equation (25) and its substitu-
tion into equation (18) we obtain the final form of the 
parameterization, which is a nonlinear algebraic equation 
for the maximum supersaturation of the cloud parcel:

$$\frac{\pi}{2} \frac{\hat{W}_0 G_{s\text{max}}}{a V} \left( \int_{s_{part}}^{s_{max}} D_p n(D_s') ds' + \int_{s_{part}}^{s_{max}} D_p n(D_s') ds' \right) - 1 = 0,$$

where

$$\int_{s_{part}}^{s_{max}} D_p n(D_s') ds' = \left( \frac{G}{a V} \right)^{1/2} \sum_{j=1}^{n_m} \frac{N_i}{s_i^j - s_i^{j-1}},$$

$$s_{max} = \frac{x}{2} \left( s_{max}^2 - x^2 \right)^{1/2} + \frac{s_{max}}{2} \arcsin \frac{x}{s_{max}},$$

$$\int_{s_{part}}^{s_{max}} D_p n(D_s') ds' = \frac{2}{3} \sum_{j-p_{part}}^{n_m-1} \frac{N_i A_i}{s_i^j - s_i^{j-1}} \ln \frac{s_i^j}{s_i^{j-1}},$$

$$+ \frac{N_i A_{max}}{s_i^{max} - s_i^{max-1}} \ln \frac{s_i^{max}}{s_i^{max-1}}.$$

where $i_{part}$ is the section boundary closest to $s_{part}$ 
(implementation of population splitting within an aerosol 
section is straightforward) and where $i_{max}$ is the boundary 
closest to $s_{max}$ with $s_{max} \leq s_{max}$ (Figure 2). The calculation 
of $s_{part}$ is carried out using either equation (28) (when $\Delta \geq 0$) 
or equation (31) (when $\Delta < 0$).

[41] The procedure for using the parameterization is 
illustrated in Figure 5. Equation (32) is solved for $s_{max}$ 
using the bisection method. All physical properties are 
evaluated at cloud base conditions. The number of droplets 
is computed from equation (8).

[42] We would like to point out that the complexity of the 
integrals in equation (32) arises from using a sectional 
representation for the CCN spectrum (equation (6)) and 
not from the procedure used to develop the parameterization 
(i.e., the concept of populations splitting and the calculation of $s_{split}$). The formulation for other size distributions (e.g., 
lognormal) can be much simpler than equation (6) but 
is beyond the scope of this paper.

5. Evaluation of New Parameterization

5.1. Activation Conditions Considered

[43] The performance of the new parameterization will be 
evaluated by comparing the predicted cloud droplet number 
centrations with those of a full numerical activation 
adibatic cloud parcel model [Nenes et al., 2001]. 
The parameterization is tested for a large number of aerosol size 
distributions and updraft velocities (about 200 cases total), 
which encompass the wide variety of tropospheric aerosols.

For convenience, size distributions are taken to be of the 
single or multiple lognormal form

$$\frac{dn(D_p)}{d \ln D_p} = \sum_{i=1}^{n_m} \frac{N_i}{\sqrt{2 \pi \ln \sigma_i}} \exp \left[ - \frac{\ln^2 (D_p/D_{g,i})}{2 \ln^2 \sigma_i} \right],$$

where $N_i$ is the aerosol number concentration, $D_{g,i}$ is the 
number mode diameter, $\sigma_i$ is the geometric standard 
development for mode $i$, and $n_m$ is the number of modes in 
the distribution.

[44] For single-mode aerosol we consider a wide range of 
number concentrations, mode diameters, and dispersions. 
The range of mode diameters and number concentrations is 
appropriate for accumulation mode particles, which 
compose most CCN. Table 1 summarizes the characteristics 
of the mode radii, number concentrations, and updrafts 
examined.

[45] For multiple-mode aerosol we have selected four of the 
Whitby [1978] trimodal representations, namely the 
marine, clean continental, average background, and urban 
aerosol representations (Table 2). The size distributions 
refer to dry size, while the chemical composition of the 
aerosol is assumed to be pure ammonium sulfate. 
To evaluate the ability of the new parameterization to capture 
the effect of surface-active organics, we also perform 
simulations for an aerosol that has the Whitby [1978] marine 
aerosol size distribution, which is assumed to be composed of 
80% (by mass) (NH₄)₂SO₄ and 20% organic that displays 
surface-active behavior. The aerosol organic component is 
a reconstruction of chemical composition observed in Po 
Valley fogs and is assumed to be composed of 18% (by 
mass) levoglucosan ($C_{6}H_{10}O_{5}$, density = 1600 kg m⁻³,
van’t Hoff factor = 1), 41% (by mass) succinic acid (C₆H₄O₄H₆, density = 1572 kg m⁻³, van’t Hoff factor = 3), and 41% (by mass) fulvic acid [U.S. Geological Survey, 1979] (C₃₃H₃₂O₁₉, density = 1500 kg m⁻³, van’t Hoff factor = 5) [Nenes et al., 2002a]. The surface tension behavior of this organic is assumed to follow the correlation of Facchini et al. [1999]. Finally, to test the performance of the parameterizations under conditions of strong kinetic limitations, we examine the same size distributions with the concentrations doubled. The characteristics of the simulations are summarized in Table 3.

Table 1. Characteristics of Single Lognormal Aerosol Distribution Runs

<table>
<thead>
<tr>
<th>Simulation Set</th>
<th>Dₚ, μm</th>
<th>Nᵢ</th>
<th>cm⁻³</th>
<th>σᵢ</th>
<th>m s⁻¹</th>
<th>E</th>
<th>Number of Points</th>
</tr>
</thead>
<tbody>
<tr>
<td>SM1</td>
<td>0.02</td>
<td>200</td>
<td>2.5</td>
<td>0.1–10.0</td>
<td>18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SM2</td>
<td>0.02</td>
<td>1000</td>
<td>2.5</td>
<td>0.1–10.0</td>
<td>18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SM3</td>
<td>0.02</td>
<td>1000</td>
<td>1.5</td>
<td>0.1–10.0</td>
<td>18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SM4</td>
<td>0.2</td>
<td>200</td>
<td>2.5</td>
<td>0.1–10.0</td>
<td>18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SM5</td>
<td>0.02</td>
<td>10000</td>
<td>2.5</td>
<td>0.1–10.0</td>
<td>18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SM6</td>
<td>0.04–0.20</td>
<td>100–1000</td>
<td>2.0</td>
<td>0.1–3.0</td>
<td>72</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Pressure is 800 mbar, and temperature is 283 K.
*SM is single mode.
*Number of simulations considered for the specified range of parameters.

Table 2. Aerosol Distribution Parameters

![Diagram](image)
and become interstitial aerosol. Droplet concentration is evaluated at 250 m above cloud base.

5.2. Comparison of New Parameterization With Parcel Model

[48] Figure 6 displays the fraction of aerosol that becomes droplets (termed as “activation ratio”) as predicted by the new parameterization and by the parcel model. For the wide variety of aerosol and updraft velocities considered the activation ratio ranges between $10^{-7}$ and 1.0. Most of the predicted values are very close to the 1:1 line and do not display significant systematic biases over the range of activation ratios; this shows that the parameterization performs well regardless of the steepness of the CCN spectrum (at low activation ratios the spectrum is steep, while at high activation ratios the spectrum is not). This also indicates that the parameterization is capable of treating highly complex and “irregular” CCN spectra, which deviate substantially from the smoothness of CCN spectra that correspond to lognormal size distributions. We do note, however, that although there is scatter about the 1:1 line, more frequently, the activated ratio tends to be underestimated. This is because the maximum supersaturation for these cases is slightly underpredicted and leads to a corresponding underprediction in droplet number. $s_{\text{max}}$ is underpredicted because the condensation rate is slightly overpredicted.

[49] Figure 7 displays the droplet number concentration as predicted by the new parameterization and by the parcel model. The range of droplet concentrations covers the entire range observed in clouds [e.g., Boucher and Lohmann, 1995; Gultepe and Isaac, 1996]. The predicted droplet number follows the 1:1 line closely. There are no regions with a variable systematic bias in the predictions, indicating that the parameterization performs well, regardless of the extent of kinetic limitations throughout the droplet population. Confirmation of this can be attained by evaluating the performance of the parameterization for the two $\Delta$ regimes. This is shown in Figure 8, which is the same as Figure 7 but with the points differentiated according to the value of $\Delta$. Most of the points examined are for $\Delta \geq 0$, but clearly, the

![Figure 6](image_url)

**Figure 6.** Fraction of aerosol that becomes droplets as predicted by the new parameterization and by the cloud parcel model.

![Figure 7](image_url)

**Figure 7.** Droplet number concentration as predicted by the new parameterization and by the cloud parcel model.

### Table 3. Characteristics of Multiple Lognormal Aerosol Distribution Simulations

<table>
<thead>
<tr>
<th>Simulation Set</th>
<th>Aerosol Type</th>
<th>Number of Points</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>TM1-M</td>
<td>marine</td>
<td>4</td>
<td>distribution from Table 2</td>
</tr>
<tr>
<td>TM1-C</td>
<td>clean continental</td>
<td>4</td>
<td>distribution from Table 2</td>
</tr>
<tr>
<td>TM1-B</td>
<td>average background</td>
<td>4</td>
<td>distribution from Table 2</td>
</tr>
<tr>
<td>TM1-U</td>
<td>urban</td>
<td>4</td>
<td>distribution from Table 2</td>
</tr>
<tr>
<td>TM2-M</td>
<td>marine</td>
<td>4</td>
<td>TM1-M concentration doubled</td>
</tr>
<tr>
<td>TM2-C</td>
<td>clean continental</td>
<td>4</td>
<td>TM1-C concentration doubled</td>
</tr>
<tr>
<td>TM2-B</td>
<td>average background</td>
<td>4</td>
<td>TM1-B concentration doubled</td>
</tr>
<tr>
<td>TM2-U</td>
<td>urban</td>
<td>4</td>
<td>TM1-U concentration doubled</td>
</tr>
<tr>
<td>TM3</td>
<td>marine</td>
<td>4</td>
<td>TM1-M concentrations; surfactant present</td>
</tr>
</tbody>
</table>

*The range in updraft velocity examined is 0.1–3.0 m s$^{-1}$. Pressure is 900 mbar, and temperature is 273 K.

*TM is trimodal; M is marine; C is continental; B is background; and U is urban aerosol.

*Number of simulations considered for the specified range of parameters.
two regimes exhibit equivalent scatter around the 1:1 line; this is a strong indication that the parameterization is insensitive to the extent of kinetic limitations.

It is important to evaluate the performance of the parameterization in predicting the parcel supersaturation (Figure 9). The range of maximum parcel supersaturations covers that predicted for most clouds; for most cases the parcel supersaturation is well captured. It is notable that the parameterization captures even the urban and background aerosols, which are subject to strong kinetic limitations (which account for roughly half of the multimodal cases examined). Particularly challenging are the TM2-U simulations. The $s_{\text{max}}$ in these cases is very small (on the order of 0.01%), and errors in this quantity can lead to large biases in predicted $N_d$; the parameterization nonetheless reproduces the parcel simulations very well. It should be noted, however, that the parameterization (for these conditions) tends to slightly underestimate $s_{\text{max}}$.

Figures 6–9 display some scatter around the 1:1 line. It is important to examine how significant this scatter is, on average and on a per case basis, as we can gain further insight into possible systematic biases. Table 4 displays the statistics of the ratio of parameterized $N_d$ to the $N_d$ calculated from the parcel model; if the parameterization perfectly captured the parcel simulations, this ratio would be 1.0. The overall average ratio is ~0.95 with a standard deviation of 0.1. Grouping the results according to aerosol case and $\Delta$ regime, we note that the performance is excellent for all the multimodal aerosols (TM1, TM2), despite the fact that about half of the cases involve significant kinetic limitations. Some of the single-mode cases perform less optimally but still are quite close to the cloud parcel predictions. The statistics for the two $\Delta$ regimes are about the same; the fact that $\Delta < 0$ has double the standard deviation of $\Delta \geq 0$ is likely a result of the smaller statistical sample. In any case, the standard deviation for all of the statistics is small, which indicates the robustness of the parameterization.

Finally, we address the performance of the new parameterization for an aerosol containing an organic species. Capturing the activation behavior of these CCN is more difficult than it is for those containing only soluble salt and insoluble substances, as the presence of an organic species within CCN can affect the activation behavior in many ways: the organic can contribute soluble material [e.g., Shulman et al., 1996], can alter the droplet surface tension [e.g., Shulman et al., 1996; Facchini et al., 1999], and can potentially affect the droplet growth kinetics [e.g., Feingold and Chuang, 2002; Nenes et al., 2002a]. Here we will focus on the solute and surface tension effects. Given that organics which can substantially affect surface tension can also be highly soluble (e.g., humic-like substances), we will assume that the organic is completely soluble (the overall effect on

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**Table 4. Statistics of the Ratio of $N_d$ Calculated From New Parameterization to $N_d$ Calculated From Parcel Model**

<table>
<thead>
<tr>
<th>Simulation Set</th>
<th>Average Ratio</th>
<th>Minimum Ratio</th>
<th>Maximum Ratio</th>
<th>Standard Deviation</th>
<th>Number of Points With $\Delta &lt; 0$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TM1(all)</td>
<td>0.9332</td>
<td>0.7242</td>
<td>1.0838</td>
<td>0.1137</td>
<td>16 (44)</td>
</tr>
<tr>
<td>TM2(all)</td>
<td>0.9159</td>
<td>0.6864</td>
<td>1.0907</td>
<td>0.1284</td>
<td>16 (56)</td>
</tr>
<tr>
<td>SM1</td>
<td>0.8819</td>
<td>0.7983</td>
<td>0.9634</td>
<td>0.0530</td>
<td>18 (0)</td>
</tr>
<tr>
<td>SM2</td>
<td>0.7923</td>
<td>0.6356</td>
<td>0.9112</td>
<td>0.0722</td>
<td>18 (0)</td>
</tr>
<tr>
<td>SM3</td>
<td>0.7333</td>
<td>0.6298</td>
<td>0.8115</td>
<td>0.0494</td>
<td>18 (0)</td>
</tr>
<tr>
<td>SM4</td>
<td>1.0204</td>
<td>0.9720</td>
<td>1.2954</td>
<td>0.0782</td>
<td>18 (5)</td>
</tr>
<tr>
<td>SM5</td>
<td>0.6955</td>
<td>0.6222</td>
<td>0.7673</td>
<td>0.0406</td>
<td>18 (5)</td>
</tr>
<tr>
<td>SM6</td>
<td>0.9780</td>
<td>0.7481</td>
<td>1.1587</td>
<td>0.0854</td>
<td>72 (26)</td>
</tr>
<tr>
<td>$\Delta &lt; 0$</td>
<td>0.9082</td>
<td>0.6864</td>
<td>1.2954</td>
<td>0.1461</td>
<td>37 (100)</td>
</tr>
<tr>
<td>$\Delta \geq 0$</td>
<td>0.9838</td>
<td>0.7975</td>
<td>1.1530</td>
<td>0.0704</td>
<td>161 (0)</td>
</tr>
</tbody>
</table>

^SM is single mode; and TM is trimodal.
activation, at least for the conditions examined here, do not change appreciably, even if the solubility changes considerably [Nenes et al., 2002a]. Under these conditions the challenge for the organic-containing CCN is to calculate the surface tension at the point of activation (which varies with aerosol size and composition). This difficulty is overcome by the sectional representation of the aerosol, as the effect of the surface-active species can be included in the calculation of the $s_i$ of each CCN section. We simulate the activation of an aerosol assumed to follow the Whitby [1978] marine aerosol size distribution (Table 2), composed of 80% (by mass) (NH$_4$)$_2$SO$_4$ and 20% (by mass) organic surfactant (with a composition as given in section 5.1). Figure 10 displays the activation ratio as a function of updraft velocity as predicted by the parameterization and by the parcel model. The parameterization captures well the activation behavior of the aerosol. Excluding the effects on surface tension results in the expected decrease in droplet number.

5.3. Comparison With Other Parameterizations

The new parameterization is tested against the performance of the Abdul-Razzak and Ghan [2000] parameterization in reproducing the results of the parcel model. These parameterizations were chosen for comparison, as they are the most comprehensive formulations available in the literature. We would like to point out that the new, the Abdul-Razzak et al. [1998], and the Abdul-Razzak and Ghan [2000] parameterizations are fundamentally different in their representation of the CCN spectrum. The former uses a sectional representation, and the latter two use a modal representation (i.e., an exact analytical integration over a lognormal size distribution). We ensured that the differences in droplet number between the parameterizations are only from their treatment of the activation process by using 200 size bins for the new parameterization (and parcel model). This way, when approximating the lognormal distribution with a series of size sections, the discretization error is very small (<1% in droplet number).

Figure 11 displays the fraction of aerosol that becomes droplets as predicted by the Abdul-Razzak and Ghan [2000] parameterization and by the parcel model. For most cases these parameterizations perform well, but numerous cases deviate considerably from the 1:1 line. This behavior is also seen in the parameterized $s_{\text{max}}$ (not shown). For a given size distribution the deviations seem to become larger as the activation fraction decreases (i.e., in the steep-slope region of the CCN activation spectrum). Figure 12 displays the droplet number for the same conditions as in Figure 11. The deviations from the 1:1 line do not seem to follow any systematic behavior, so they are less likely to be controlled by kinetic limitations (this is understandable, as the parameterization is fitted to numerical parcel simulations, thus implicitly accounting for kinetic limitations). Actually, the opposite is occurring: the predictions for the marine aerosols deviate notably from the parcel simulations. Abdul-Razzak and Ghan [2000] report that errors are expected from the parameterization when the modal diameters differ by about an order of magnitude. The nuclei and accumulation modes in the marine and continental aerosol runs vary by a factor of 7 and for the urban and background aerosol by a factor of 5; therefore errors are expected. The deviations do not seem to be focused in any particular region of droplet number concentration but rather for certain combinations of mode dispersion and updraft velocity. This behavior indicates that
6. Conclusions

[55] A new aerosol activation parameterization has been developed based on a generalized sectional representation of aerosol size and composition. The maximum supersaturation needs to be determined first by numerically solving an algebraic equation, and then the droplet number concentration is computed from the supersaturation spectrum. The flexibility of the parameterization and the comprehensive treatment of the droplet activation justify the additional computational effort.

[56] We introduce the concept of “population splitting,” in which the CCN that form droplets are divided into two separate populations: those which have a size close to their critical diameter and those that do not. We also explicitly introduce kinetic limitations on droplet growth. For a wide range of CCN activation conditions the parameterization is free from any empirical information or correlations derived from detailed numerical simulations. There are certain conditions for which an empirically derived correlation is utilized; this is required whenever most of the activated CCN are kinetically limited. Whether the empirical information is needed or not is determined by a parameter that indicates the extent of kinetic limitations (defined as the “discriminant criterion,” $\Delta$).

[57] Predictions of the parameterization are extensively compared against those of a detailed cloud parcel activation model for a variety of aerosol activation conditions that cover a wide range of chemical variability and CCN concentrations. The parameterization closely tracks the parcel model simulations, while the computational burden of the parameterization is more than 3 orders of magnitude less than that of the parcel model itself. The new parameterization displays superior performance in both accuracy and robustness when compared to existing parameterizations. Decreased reliance on empirical information does not diminish the performance of the parameterization; on the contrary, it seems to enhance its robustness.

[58] The new parameterization, in the formulation presented in this paper, can treat all types of aerosol that follow Köhler theory; as no restriction of an explicit link between dry size and critical supersaturation is needed, the parameterization can treat internally or externally mixed aerosol with size-varying compositions and includes the effects of surface-active species (organics), insoluble species, and slightly soluble species. The current formulation can even treat recently identified effects, such as the heating of CCN from the presence of black carbon [Conant et al., 2002; Nenes et al., 2002b]. The possibilities do not stop here. The structure of the parameterization allows for further extension, such as explicit treatment of condensable gases and organic species that exhibit slow growth kinetics and including entrainment in the parcel (nonadiabatic activation). Although much is still unknown about the effect of organic species on droplet activation, the ability to parameterize their possible effects is highly desirable, as it establishes the framework for a comprehensive assessment of the aerosol indirect effect in global climate models.

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A. Nenes, Schools of Earth and Atmospheric Sciences and Chemical Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA. (nenes@eas.gatech.edu)

J. H. Seinfeld, Department of Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, USA. (seinfeld@caltech.edu)