A simple analytical model of aerosol properties with account for hygroscopic growth. Equilibrium size spectra and cloud condensation nuclei activity spectra

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Abstract. A microphysical model of aerosol size spectra that includes hygroscopic growth is presented. In the presence of atmospheric humidity, an aerosol size spectrum of the Junge [1952] type transforms into a superposition of two equilibrium power law spectra, with indices determined by the original Junge index and the fraction of soluble material contained in the aerosol. The aerosol size distributions are presented as explicit functions of relative humidity $H$ for three different humidity regimes: (1) moderate humidity, (2) high humidity but subsaturation, and (3) interstitial cloud aerosol. On the basis of this model of aerosol hygroscopic growth, the Twomey [1959] cloud condensation nuclei (CCN) power law is then derived so that its coefficients are related to the aerosol microstructure and humidity dependence under subsaturation. This simple aerosol model can be used in cloud and climate models that do not treat explicitly CCN activation and for evaluation of aerosol optical properties. An application for aerosol optical properties is considered by Khvorostyanov and Curry [this issue].

1. Introduction

Improved understanding of the role of atmospheric aerosol in climate change, air quality, acid deposition, biogeochemical cycles, visibility reduction, and cloud and precipitation processes requires consideration of the hygroscopic growth of aerosol in the presence of atmospheric water vapor. The climatic impact of aerosols through their impact on the Earth's radiation budget has been an issue of particular concern in recent years [e.g., Charlson et al., 1992; Twomey, 1993; Curry et al., 1995; Federal Aviation Administration-International Global Atmospheric Chemistry Program (FAA IGAC), 1996].

In the presence of water vapor, the size of an aerosol particle may increase over the humidity range 30-95% by 2-10 times over its original "dry" size, depending on aerosol composition [e.g., Kasten, 1969; Georgievsky and Rosenzweig, 1973; Hanel, 1976; Fitzgerald et al., 1982; Hegg et al., 1996]. For the numerous applications requiring accurate consideration of the size spectra of aerosols, a general functional relationship is desired that relates the dry aerosol size spectrum, the fraction of aerosol that is soluble, and atmospheric relative humidity to determine the equilibrium spectra of the "wet" aerosol.

Kasten [1969] derived an empirical relation between the size of a dry aerosol particle $r$ and the equilibrium size of an aqueous solution droplet $r^*$ to be of the form

$$ r^*(H) = r(H_0)(1 - H)^{-k} $$

(1)

where $H$ is the ambient relative humidity, $H_0$ is the threshold relative humidity for deliquescence, and $k = 0.26$ was chosen by Kasten as a fit to empirical data. A drawback of the Kasten relationship is that the coefficient $k$ varies with aerosol composition.

Hanel [1976], on the basis of measurements of the relation of the dry aerosol mass to accumulated water in a particle as a function of relative humidity, suggested a semiparametric formula where the increase of the equilibrium radius was expressed through this relation and parameterized with some empirical tabulated function of $H$. He constructed six empirical models of the wet aerosol of different types and showed good agreement with his approach with Kasten's [1969] parameterization (1) for index $k \approx 0.2-0.3$, depending on aerosol type. Fitzgerald [1975] derived approximate relations describing the variation with relative humidity of the equilibrium size of aqueous solution droplets for a chemically homogenous aerosol as a function of relative humidity between 81% and 99.5%.

An analytical expression for the wet aerosol size distribution at high humidity $H = 1$ with soluble fraction containing ~20% NaCl was obtained by Levin and Sedlazov [1966] and used for numerical studies of Twomey [1959] cloud condensation nuclei (CCN) activation in clouds. Unfortunately, this distribution is rather complicated and difficult to use in derivation of simple analytical relationships for optical parameters. However, this approach can be generalized for a wider range of humidities and various aerosol chemical compositions and then reduced to the superposition of the power laws, which creates the appropriate basis for the simple evaluation of aerosol optical properties.

Over the last 2 decades, many numerical aerosol models have been developed, including rather sophisticated approaches with
detailed calculations of the aerosol particle growth from the gaseous phase and cloud processing of the aerosol [e.g., Hegg, 1990; Kaufman and Tarpley, 1994]. Recently, recognition of the strong effect of atmospheric aerosol on the global radiative balance and its potential counteraction of greenhouse gas-induced global warming has led to a new focus on atmospheric aerosol [FAA-IGAC, 1996].

To address these issues, some simple yet accurate functional relationships are derived in this paper for the humidity dependence of microphysical properties of the aerosol. We apply methods developed in cloud physics [e.g., Twomey, 1959; Bitov, 1961; Levin and Seddonov, 1966; Mason, 1971; Pruppacher and Klett, 1997] to derive simple yet accurate analytical formulas for calculation of the hygroscopic growth of the aerosol equilibrium radius and size spectra. Our analytical expressions are suitable for both the cloudless and cloudy atmosphere, can account explicitly for different aerosol compositions and are valid for values of moderate humidity, high humidity but subsaturated, and interstitial cloud aerosol. The model is then related to the Twomey [1959] CCN power law, and its coefficients are related to the aerosol microstructure and humidity dependence under subsaturation. Application of this model to determination of aerosol optical properties is given by Khorostyanov and Curry [this issue]; in particular, the use of these functional relationships allows derivation of simple expressions for scattering and absorption coefficients.

2. Dry Aerosol Size Spectrum and Soluble Fraction

The size spectrum of atmospheric aerosol is often approximated by a superposition of two or more lognormal distributions which characterize different sources of aerosol. Geographically and climatologically averaged background aerosol can be described sufficiently well by the Junge [1952] size distribution

\[ f(r_d) = a_d r_d^{-\mu} \]  

where \( r_d \) is the aerosol radius, \( f(r_d) \) is the aerosol size distribution, and the subscript \( d \) refers to the dry aerosol. The parameter \( \mu \) is a constant that determines the variation of aerosol concentration with radius. The parameter \( a_d \) in (2) is related to the total aerosol concentration \( N \)

\[ N = \int_{r_{\text{min}}}^{r_{\text{max}}} f_d(r_d) dr_d \]  

by substituting (2) into (3) and integrating to obtain

\[ a_d = N (\mu - 1) \left( 1 - \left( \frac{r_{\text{min}}}{r_{\text{max}}} \right)^{\mu - 1} \right) \]  

The term \( r_{\text{min}}^\mu \) is much less than unity and can usually be neglected.

In the presence of atmospheric water vapor, the equilibrium size distribution of aerosol which contains a fraction of soluble matter is modified by deliquescence. The size distribution of the wet aerosol is determined by a balance of the solution effect, which tends to decrease saturation vapor pressure \( e_s(r) \) near an aerosol particle, and the surface tension force (curvature effect), which tends to increase \( e_s(r) \). Accounting for these two competing effects, the expression for \( e_s(r) \) of an aerosol particle with radius \( r \) can be written in the form [e.g., Pruppacher and Klett, 1997]

\[ e_s(r) = e_s(\infty) \exp \left( - \frac{\nu \Phi m_r M_w}{M_d (4\pi/3) \rho_w r^3 - m_d} \right) \exp \left( \frac{B}{r} \right) \]  

where \( e_s(\infty) \) is the saturation vapor pressure over a plane surface of pure water, \( \nu \) is the first exponent describes solution effects and the second exponent describes the effects of curvature. Here \( \nu \) is the number of ions in a solution, \( \Phi \) is the molal osmotic coefficient, \( m_r \) is the mass of dry aerosol that is soluble, \( M_d \) and \( M_w \) are molecular weights of the soluble portion of the dry aerosol and water, respectively; and \( \rho_w \) is the density of pure water (we assume a dilute solution). The term \( B = 2 \alpha \Pi(R,T \rho_w) / \kappa \) is the Kelvin parameter, \( \alpha \) is surface tension at the vapor-solution interface, \( \Pi \) is the specific gas constant for water vapor, and \( T \) is temperature. Since we are concerned with the equilibrium size of a wet aerosol, we can assume that the solution is dilute and that \( B r \ll 1 \), implying that \( e_s = 2 \) and \( (4\pi/3) \rho_w r^3 >> m_d \). We can then do a first order expansion of (5) to obtain

\[ e_s(r) = e_s(\infty) \left[ 1 + \frac{B}{r} - \frac{A}{r} \right] \]  

where \( A \), called the nuclei activity, describes the solute effect and is given as

\[ A = 2 \frac{M_w}{M_d} \frac{3m_d}{4\pi \rho_w} \]  

Only the soluble portion of the total aerosol mass interacts with the atmospheric water vapor. As was first pointed out by Junge [1957], most individual atmospheric aerosol particles are of a mixed chemical nature and contain both water-soluble and water-insoluble substances. As summarized by Pruppacher and Klett [1997], the water soluble mass fraction in atmospheric aerosol particles has been observed to vary from 0.1 to 1.0. Maritime air generally consists of a soluble fraction between 0.8-1.0, while continental air typically has a soluble fraction that is less than 0.6.

To account for variations in soluble mass fraction, we parameterize \( A \) to be of the form [following Levin and Seddonov, 1966]

\[ A = h (r_{\text{d}})^{2(1+\beta)} \]  

where the parameters \( h \) and \( \beta \) depend on the chemical composition and physical properties of the soluble part of an aerosol particle. The parameter \( \beta \) describes the soluble fraction of an aerosol particle as follows: when \( \beta = 0.5 \), the soluble fraction is proportional to the volume of the aerosol particle; when \( \beta = 0 \), the amount of soluble fraction is proportional to the particle surface area; and when \( \beta = -1 \), the amount of soluble fraction does not depend on the size of the aerosol particle. Measurements have shown that the amount of aerosol soluble mass fraction may decrease with increasing particle radius [e.g., Lekhtman, 1972; Mexinaros, 1978], implying a decrease of \( \beta \) with \( r \), and \( \beta \) can therefore be between 0.5 and 0. In order to clarify the meaning of the parameter \( h \), we consider the two cases \( \beta = 0.5 \) and \( \beta = 0 \).

1. In the case where \( \beta = 0.5 \), the soluble fraction is proportional to the volume. Under the assumption that the soluble fraction of the aerosol mass \( m_s \) is proportional to the aerosol volume, we can write
\[ m_d = Q_w \rho_d \frac{A}{3} \pi r_d^3 \]  

where \( Q \leq 1 \) is the volume fraction of the soluble part of the aerosol and \( \rho_d \) and \( r_d \) are the density and radius, respectively, of the dry aerosol particle. Substituting (9) into (7), we obtain

\[ A = 2Q_w \rho_d \frac{r_d^3}{\rho_w} \frac{M_w}{M_d} \]  

Equating this expression to (8), which becomes, for this case, \( A = b r_d^2 \), we obtain for \( b \)

\[ b = 2Q_w \rho_d \frac{M_w}{\rho_w} \frac{M_d}{M_d} \]  

For \( \beta = 0.5 \), the term \( b \) is a dimensionless parameter, and its value depends on the chemical composition of aerosol and the volume fraction of the soluble part. Some characteristics of NaCl and ammonium sulfate are presented in Table 1, which shows that if the soluble material is NaCl, \( b = 1.33 \) for fully soluble nuclei (\( Q = 1 \)) and \( b = 0.26 \) for \( Q = 0.20 \). If the soluble material is ammonium sulfate, \( (NH_4)_2SO_4 \), then \( b = 0.505 \) for fully soluble nuclei (\( Q = 1 \)) and \( b = 0.25 \) for \( Q = 0.5 \). In the calculations below, we use the value \( b = 0.25 \), which may correspond to the dry aerosol containing 50% ammonium sulfate, as found by Handel [1976] in measurements of continental and marine (Atlantic) aerosols, or 20% NaCl, as was assumed by Junge [1963]. All of the results herein can be easily recalculated for any other value of \( Q \), or for any other chemical composition using appropriate values of \( M_w \) and \( \rho_w \).

2. In the case where \( \beta = 0 \), the soluble fraction is proportional to the surface area. In this case, the proportion of the soluble material in the dry aerosol can be parameterized as

\[ Q_w(r_d) = Q_w \frac{4\pi r_d^2}{r_d} \]  

where \( r_w \) is some scaling radius and \( Q_w \) is a dimensionless parameter characterizing the soluble fraction of aerosol at \( r_d = r_w \). Equation (12) implies that the soluble fraction in a dry nucleus is inversely proportional to the particle radius; that is, the soluble fraction decreases with radius as the surface to volume ratio decreases, while the insoluble fraction increases. This parameterization is consistent with the formation of accumulation mode aerosol (0.1 < \( r < 1 \) \( \mu \text{m} \)) from the gaseous phase on the surface of a previously insoluble particle (e.g., mineral and dust), or it can serve as a parameterization of a multicomponent aerosol mixture where the admixture of insoluble fraction increases with radius. Using (12), we can write

\[ m_d = Q_w(r_d) \left( \frac{4\pi}{3} \right) \rho_d r_d^3 = Q_w \left( \frac{4\pi}{3} \right) \rho_d r_d r_d^2 \]  

That is, the mass of the soluble portion of the aerosol is proportional to the squared radius (surface area) of the droplet. Equations (7) and (13) can be combined into

\[ A = \frac{3}{4} \frac{M_w}{M_d} = 2Q_w \rho_d \frac{M_w}{\rho_w} \frac{M_d}{M_d} r_d r_d^2 = b r_d^2 \]  

where

\[ b = 2Q_w \rho_d \frac{M_w}{\rho_w} \frac{M_d}{M_d} r_d r_d \]  

(15)

The term \( b \) in (15) has the dimension of length as it is proportional to the scaling radius \( r_d \).

Figure 1 shows the masses of the soluble part of the dry nuclei for the volume-proportional fraction (solid curve) and surface-proportional soluble fraction for three different values of the threshold radius: \( r_{th} = 0.01, 0.02, \) and \( 0.05 \) \( \mu \text{m} \). According to Figure 1, the masses of surface-proportional soluble fraction are by 1-2 orders of magnitude less than the mass of the volume-proportional soluble fraction in the region of \( 0.1 < r < 1 \) \( \mu \text{m} \), as their increase with radius is much slower. This causes higher activity of the nuclei with \( \beta = 0.5 \).

In this paper, we primarily consider \( \beta = 0.5 \). Note, however, that all the calculations can also be done for the soluble fraction proportional to the surface, and the differences between the cases with \( \beta = 0.5 \) and \( \beta = 0 \) are also discussed in section 3.

3. Equilibrium Radius and Wet Aerosol Size Spectrum

Denoting the vapor pressure in the environment by \( e \), the supersaturation \( S(r) \) is given by

\[ S(r) = \frac{e}{e(r)} - 1 \]  

and the supersaturation \( S(\infty) \) over a plane surface of pure water is given by

\[ S(\infty) = \frac{e}{e(\infty)} - 1 \]  

Using (16) and (17), we can write (6) as

\[ \frac{S(\infty) + 1}{S(r)} = 1 + \frac{A}{r} = \frac{1}{r} \]  

(18)

For unsaturated conditions, we can write a relation between negative environmental supersaturation \( S(\infty) \) (strictly speaking, subsaturation) and environmental relative humidity \( H = e / e(\infty) \):

**Figure 1.** Masses of dry nuclei for the volume-proportional soluble fraction (solid curve) and surface-proportional soluble fraction for three values of the threshold radius: \( r_{th} = 0.01, 0.02, \) and \( 0.05 \) \( \mu \text{m} \).
The equilibrium radius \( r^*(H) \) for a wet aerosol particle can be determined by solving the cubic equation (18) with the condition \( S(r) = 0 \). Introducing the new variable \( y = r^0 \) and using (19), (18) can be written as an incomplete cubic equation

\[
y^3 - \left( \frac{B}{A} \right) y + \left( \frac{H - 1}{A} \right) = 0
\]

(20)

where \( A \) is the activity and \( B \) is the Kelvin constant. The positive real root of the solution to (20) gives the following expression for \( r^*(H) \):

\[
r^*(H) = b^{1/3} r^0 \left( \frac{1}{2} + \frac{1}{2} (1 - H)^{1/3} \left[ 1 + \frac{R}{(3A)^{1/3}} \right] (1 - H)^{2/3} \right)^{-1}
\]

(21)

Figure 2 shows the relative variation of the equilibrium radius \( r^*(H)/r_0 \) for \( \beta = 0.5, b = 0.25, \) and varying values of \( H \). These theoretical curves are compared with Kasten [1969, equation (1)], who chose \( k = 0.26 \) as a fit to empirical data. From Figure 2, we can draw the following conclusions: (1) The presented model is in good agreement with Kasten's [1969] model and empirical data and (21) satisfactorily describes the hygroscopic growth of aerosol particles with increasing humidity. (3) The best agreement with Kasten's [1969] curve is seen for the values of \( r_0 = 0.02 \mu m \); this may be characteristic of a continental aerosol with a soluble fraction that is not very high. Marine aerosol with a larger soluble fraction \( (r_0 = 0.05 - 0.2 \mu m) \) in Figure 2 may exhibit much faster hygroscopic growth, especially at high humidities \( H > 0.8 - 0.9 \mu m \). (3) The difference among the curves with different soluble fraction is rather small (10-15%) for \( H \leq 0.7 \), but at higher humidities, \( H > 0.9 - 0.95 \), the larger particles (with larger \( r_0 \) grow much faster and the difference reaches 50-70%. This difference arises from the second term in (21), whose contribution increases with relative humidity. This prevailing growth of larger particles at very high humidities was noted by Junge [1963], which is shown herein to lead to a decrease in slopes of the size spectra at \( H \sim 1 \).

Figure 2. Relative increase of equilibrium radius with humidity calculated from (21) for four values of dry radius \( r_0 \), compared with Kasten [1969, equation (1)].

Hence this simple analytical aerosol model with few parameters provides a satisfactory description of the hygroscopic growth of the individual aerosol particles and is in agreement with experimental data [e.g., Hanel, 1972; 1976; Fitzgerald, 1975] and with Kasten’s [1969] approximation. Additionally, (21) along with (9)-(15) can be used to predict the dependance of equilibrium radius as a function of relative humidity directly in terms of the aerosol microstructure. Note that, strictly speaking, this approach might have increasing errors for \( H < 0.6 \) since we consider dilute solutions and the mechanism of particles growth can be different at lower humidities (e.g., capillary adsorption); however, this parameterization is still useful in a region of lower humidities.

We can derive the size distribution of wet aerosol \( f(r) \) in terms of the dry aerosol spectrum and a spectrum of aerosol activity \( f_A(A) \). Because the total aerosol concentration is constant, we can write

\[
f_A(A) dA = f_A(r_0) dr_0
\]

(22)

\[
f(r) dr = f_A(A) dA
\]

(23)

Substituting (2)-(4) for the Junge [1952] distribution into (22) and incorporating (8), we obtain the following spectrum of aerosol activity:

\[
f_A(A) = c_A A^{-F}
\]

(24)

where

\[
c_A = N_0 \left( \frac{\mu + 1}{\mu + 1} \right) r_{min}^{\mu+1} \beta^{\mu+1} \frac{\beta \mu + \beta + 1}{2(1 + \beta)}
\]

(25)

\[
F = \frac{\mu + 1}{\mu + 1} b^{\beta + 1} \beta^{\mu+1} \frac{\beta + 1}{2(1 + \beta)}
\]

(26)

| Table 1. Characteristics of Soluble Part Consisting of NaCl and Ammonium Sulfate |
|-----------------|--------|----------|--------|---------|
| Soluble Material | Molecular Weight \( M_w \) \( g \) mol\(^{-1}\) | Density \( \rho_w \) \( g \) cm\(^{-3}\) | Parameter \( b \) | \( Q_1 = 1 \) | \( Q_2 = 0.2 \) |
| NaCl            | 50.5   | 2.16     | 1.33   | 0.25    |
| (NH₄)₂SO₄       | 132    | 1.77     | 0.3    | 0.25    |

\( Q_1 = 1 \) is fully soluble nuclei, while \( Q_2 = 0.2 \) is partially soluble nuclei.
The expression (24) is a power law of the same form as (2), with index \( r \).

The equilibrium aerosol size distribution \( f(r) \) is derived by assuming \( S(r) = 0 \) (the condition of aerosol in equilibrium with environment). We can write (23) as

\[
 f(r) = j_n \left(A \frac{dA}{dr}\right) \tag{27}
\]

Differentiating the function \( A(r) \) from (8) and incorporating this expression along with (18) into (27), we obtain

\[
 f(r) = C r^{-\mu_{\text{wet}}} \left[ 1 - S(\infty) \right]^{-\frac{\mu_{\text{wet}}}{R}} \left( 1 - \frac{3}{2} S(\infty) \right) \left[ \frac{\mu_{\text{wet}} + \beta}{1 + \beta} \right] \tag{28}
\]

where we introduce two new indices \( \mu_{\text{wet}} \) and \( \mu_{\text{dry}} \).

\[
 \mu_{\text{wet}} = \frac{3\mu + 2\beta - 1}{2(1 + \beta)} \quad \mu_{\text{dry}} = \frac{\mu + \beta}{1 + \beta} \tag{29}
\]

It will be shown below that \( \mu_{\text{wet}} \) represents the index of the modified Jeune [1959] power law for the equilibrium aerosol in an unsaturated atmosphere and that \( \mu_{\text{dry}} \) is the index of the power law of aerosol size spectrum at relative humidity \( H = 100\% \) in a cloud that is in equilibrium with the droplets. The parameter \( C \) is determined to be

\[
 C = N \frac{\mu_{\text{wet}} - 1}{1 + \beta} \min \left( \frac{b}{R}, \frac{b}{2(1 + \beta)} \right) \tag{30}
\]

The expression (28) can be simplified and reduced to a power law in the following way. Note that over the range of humidities \( H < 0.97 \), the term \( X = -S(\infty) R/B = (1 - H) rB \) is much greater than unity. Even for \( H = 0.95 \) with \( B = 1.2 \times 10^{-3} \mu \), we have \( X > 1 \) for \( r > 2.10^{-3} \mu \). Therefore, for further transformations, it is convenient to write the terms of the form \((1 + X)\) in (28) in the form \( X(1 + 1/X) \), and we can rewrite (28) as

\[
 f(r) = C r^{-\mu_{\text{wet}}} \left[ X \right]^{-\left(\mu_{\text{wet}} - \mu_{\text{dry}}\right) + 1} \left[ 1 + \frac{1}{X} \right]^{-\frac{\mu_{\text{wet}}}{R} \left(\mu_{\text{wet}} - \mu_{\text{dry}}\right) + 1} \frac{3X}{2} \left[ 1 + \frac{2}{3} X \right] \tag{31}
\]

We can expand the second bracket in (31) into a power series by the small parameter \( X \ll 1 \), and multiplying the second and third brackets, keeping only the terms of the order of \( X^2 \), and neglecting the terms of the order of \( X^3 \ll 1 \), we can write (31) as

\[
 f(r) = C r^{-\mu_{\text{wet}}} \left[ X \right]^{-\left(\mu_{\text{wet}} - \mu_{\text{dry}}\right) + 1} \left[ 1 \right] \left(\mu_{\text{wet}} - \mu_{\text{dry}}\right) + 1 \frac{1}{X} \frac{2}{3} X \tag{32}
\]

Substituting (30) for \( C \) into (32) and introducing a new parameter \( R = \mu_{\text{wet}} - \mu_{\text{dry}} \) we obtain, after some simple transformations and substitution for \( X \),

\[
 f(r) = 3 N \mu_{\text{min}} \left(\frac{b}{1 - H} \right) R \left[ r^{-\mu_{\text{wet}}} \right] \left( R + 1 \frac{1}{3} \frac{B}{(1 - H)} \right) \tag{33}
\]

The power index for the wet aerosol \( \mu_{\text{wet}} \) is given by (29) and the index \( R \)

\[
 R = \frac{H - 1}{\gamma(1 + \beta)} \tag{34}
\]

determines explicitly the relative humidity dependence of the size spectrum. The distribution (33) is a superposition of two power laws with indices \( \mu_{\text{wet}} \) and \( \mu_{\text{dry}} + 1 \).

The expression of (28) into a power series by \( X^2 \) becomes invalid when \( H \) approaches unity since the value \( X^2 \) becomes much larger than unity and the expression (33), proportional to \((1 - H)^2 \), would give infinite values. However, in this case, we can neglect the terms with \((1 - H) \) in (28) and obtain the size spectrum for the case when \( H \sim 1 \)

\[
 f(r) = N \mu_{\text{min}} \left(\frac{1}{2(1 + \beta)} \right) R \left[ R^{-\mu_{\text{wet}}} \right] \tag{35}
\]

where \( \mu_{\text{dry}} \) is defined by (29) and \( R \) is defined by (34). Expression (35) is also a power law distribution.
Using the same normalization condition as (3) but substituting (33) into (3), we obtain for the lower boundary $r_{\text{min}}$ at moderate humidity $H < 0.95$:

$$r_{\text{min}} = r_{\text{min}}^{(\mu - 1)/\mu_{\text{at}} - 1} \left[ \frac{3}{2(1 + \beta)} \left( \frac{b}{H} \right)^{\mu - 1} \left( 1 - H \right) \right]^{1/((\mu_{\text{at}} - 1))}$$  \hspace{1cm} (36)

In the same way, substituting (35) into the integral (3), we obtain for the lower boundary at $H \rightarrow 1$

$$r_{\text{min}} = r_{\text{min}}^{(\mu - 1)/\mu_{\text{at}} - 1} \left[ \frac{6}{2(1 + \beta)} \left( \frac{b}{H} \right)^{\mu - 1} \left( 1 + \beta \right) \right]^{1/((\mu_{\text{at}} - 1))}$$  \hspace{1cm} (37)

The existence of these limits means that the aerosol size spectra not only change their slopes during deliquescence but also are displaced as a whole toward larger radii, so that the former lower limit is displaced to the larger radii owing to swelling since we do not assume formation of the new small particles during deliquescence. If we assume that $\mu_{\text{at}} = 0.1 \mu m$ for dry aerosol, then estimations from (36) with $\beta = 0$ give $r_{\text{min}} \approx 0.12 - 0.14 \mu m$ for $H < 0.95$. Estimations with (37) show that for $H \rightarrow 1$, the increase in lower limit can be as large as $0.3 - 0.35 \mu m$ for $\beta = 0.5$.

So, over the entire range of atmospheric humidity, the expressions for the size distribution of wet aerosol, (33) and (35) take the form of a power distribution in $r$. Figure 3 shows very good agreement between the size spectra calculated with the exact (28) (Figure 3a) and approximate (33) and (35) (Figure 3b) for both moderate humidity and $H = 1$. It is seen from Figure 3 that the slope of the spectra remains the same for $H \leq 0.95$ but decreases as $H \rightarrow 1$.

The indices of both power distributions (33) and (35) are presented in Table 2, which shows that the indices vary for the two different relative humidity ranges (moderate humidity, $H < 0.95$, and very high humidity, $H = 1$) and also according to whether the soluble fraction of the aerosol is proportional to the particle volume or the particle surface area.

If the soluble aerosol fraction is proportional to volume ($\beta = 0.5$), then $\mu_{\text{at}} = \mu$. For conditions of moderate humidity, $\mu_{\text{at}} = \mu$. Figure 3 illustrates that the slope of the size spectra does not change for varying values of relative humidity $H$. A contrasting situation is seen when the soluble aerosol fraction is proportional to the surface area ($\beta = 0$), whereby $\mu_{\text{at}} = (3\mu - 1)/2$ and $\mu_{\text{at}} < \mu$. For this case, the slope of the size spectra increases: $\mu_{\text{at}} = 4, 5.5$, and $7$ for the values $\mu = 3, 4, 5$, respectively. We emphasize that the change of indices for both $\beta = 0$ and $\beta = 0.5$ is not smooth for increasing humidity. Instead, this change occurs as a fast, sharp transition from the dry size spectra to the wet spectra by adding moisture to the dry aerosol, such as the swelling that would occur in an expansion chamber. Then the slopes of the spectra do not change during increasing humidity until $H > 0.95$, when the greater growth of the largest particles results in changed slopes.

Figure 3c illustrates three size spectra for $\beta = 0$ (with various values of $\mu_{\text{at}}$), in comparison with the case $\beta = 0.5$. It is seen that (1) the increase in radius due to deliquescence (increasing $H$ in the case of $\beta = 0$ is larger for larger $r_{\text{at}}$ (i.e., relative amount of soluble fraction) and (2) the slope in all cases with $\beta = 0$ ($\mu_{\text{at}} = 5$) is larger than that for $\beta = 0.5$ ($\mu_{\text{at}} = 4$). So this parameterization accounts for the fact that smaller particles with $\beta = 0$ undergo larger hygroscopic growth (thereby increasing the slope of the size spectra) because they have a larger relative amount of soluble fraction, while the growth of the larger particles is diminished by the smaller soluble fraction as illustrated in Figure 1.

For $H \rightarrow 1$, if $\beta = 0.5$ and $\mu > 1$, then $\mu_{\text{at}} < \mu$ and the slope of the size spectrum of wet aerosol is less than that of dry aerosol (see Table 2). For $\beta = 0$, then $\mu_{\text{at}} = \mu$ and the slope of the size spectrum of wet aerosol at $H \rightarrow 1$ is equal to that of dry aerosol.

So the general behavior of the power law indices is different for different ranges of humidity. We can identify the following three regimes as shown in Table 2: (1) completely dry aerosol can be characterized by $\mu$, with the soluble fraction proportional to the particle volume or surface; (2) for moderate relative humidity ($H < 0.95 - 0.97$), the indices are determined by $\mu_{\text{at}}$ in (16) and for $\beta = 0.5$, the indices remain the same and $\mu_{\text{at}} = \mu$, while for $\beta = 0$, then $\mu_{\text{at}} > \mu$; and (3) for extremely humid conditions, when $H \rightarrow 1$, the indices are determined by $\mu_{\text{at}}$ in (16) and $\mu_{\text{at}} < \mu$; for $\beta = 0.5$, the index is $\mu_{\text{at}} < \mu$, and for $\beta = 0$, the index is $\mu_{\text{at}} = \mu$. Thus we have two sharp, almost step-like transitions in aerosol size spectra and their power indices with varying relative humidity at the deliquescence point and at very high humidity with prevailing growth of the large particles.

The reason for the existence of these two different humidity regimes is apparent from the structure of (33) and (35). For moderately high values of relative humidity, the main govern-

| Table 2. Power Indices of Aerosol Size Spectra for Two Regimes of Humidity $\mu_{\text{at}}$ and $\mu_{\text{at}}$ for Varying Volume-Soluble Fraction and Varying Values of the Junge [1959] Index $\mu$ for Dry Aerosol |
|-----------------|-----------------|-----------------|-----------------|-----------------|
|                | 3               | 3.5             | 4               | 4.5             |
| $\beta = 0.5$  | $\mu_{\text{at}}$ | $\mu_{\text{at}}$ | $\mu_{\text{at}}$ | $\mu_{\text{at}}$ |
| $\beta = 0$    | 3               | 3.5             | 4               | 4.5             |
| $\beta = 0.5$  | 2.33            | 2.67            | 3               | 3.33            |
| $\beta = 0$    | 3               | 3.5             | 4               | 4.5             |
| $\beta = 0.5$  | 3.67            | 3.67            | 5               | 5               |

<table>
<thead>
<tr>
<th></th>
<th>$\mu_{\text{at}}$</th>
<th>$\mu_{\text{at}}$</th>
<th>$\mu_{\text{at}}$</th>
<th>$\mu_{\text{at}}$</th>
</tr>
</thead>
<tbody>
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<td>$\beta = 0.5$</td>
<td>$\mu_{\text{at}}$</td>
<td>$\mu_{\text{at}}$</td>
<td>$\mu_{\text{at}}$</td>
<td>$\mu_{\text{at}}$</td>
</tr>
<tr>
<td>$\beta = 0$</td>
<td>3</td>
<td>3.5</td>
<td>4</td>
<td>4.5</td>
</tr>
</tbody>
</table>
4. Interstitial Cloud Aerosol and CCN Supersaturation Spectrum

In section 3, we considered the growth of aerosol up to the point where the haze particle becomes activated ($H \sim 1$). To complete the picture, we consider the aerosol in cloud, i.e., under weak supersaturation, $S > 0$. All the arguments used when deriving (28) are valid also for this case; thus (28) is valid also for the size spectrum of cloud aerosol. For a typical cloud, $S << 1$ and the parameter $|\kappa| = S R_b << 1$. Then expanding (28) by the small parameter $\kappa$ and using the relation $R = 1 - \kappa$ and the normalization constant $C$ from (30), we obtain

$$f(r) = Cr^{-\beta_b} \left[1 - \left(1 - \frac{1}{2} \right) S R_e \left(\frac{R_e}{B} \right)^{1 - \frac{3}{2}}\right]$$

$$- Cr^{-\beta_b} \left[1 - \left(R - \frac{1}{2} \right) S R_e \left(\frac{R_e}{B} \right)^{1 - \frac{3}{2}}\right] = 2 NR_{\min} \left(\frac{h B}{B} \right)^{R e - \beta_b} \left[1 - \left(R - \frac{1}{2} \right) S R_e \left(\frac{R_e}{B} \right)^{1 - \frac{3}{2}}\right]$$

(38)

representing a boundary between activated nuclei with $r > R_b$, which have transformed into droplets and unactivated nuclei with $r < R_b$. The value of $R_b$ is determined by supersaturation $S(\infty)$ as defined by (39).

An example of interstitial aerosol size spectra is given in Figure 4, calculated with (38) for three values of supersaturation, $S = 0.1, 0.01$, and $0.005\%$. Figure 4 shows that the slopes of all spectra are almost the same ($\mu_e = 3$), except for the slight decrease near the right boundary caused by the second term in (38), which is positive for $S > 0$. The size spectra in Figure 4 are limited by the three different boundary radii that vary with the value of the supersaturation. A simple estimation with Kelvin’s parameter $B = 1.2 \times 10^{-3} \mu m$ gives $r_e = 0.75 \mu m$ at $S = 0.1\%$, but $r_e = 7.5 \mu m$ at $S(\infty) = 0.01\%$ and $r_e \sim 15 \mu m$ at $S(\infty) = 0.005\%$. Thus the equilibrium CCN size spectrum in a cloud may spread to sizes greater than $5 \mu m$ and overlap with the droplet spectrum since these large nuclei are not activated at small supersaturation (although they can be activated at larger supersaturation).
To illustrate this overlapping in more detail, we calculated a superposition of the interstitial aerosol spectra and a droplet size spectrum in the form of a gamma distribution with the index $p = 6$ and a mean droplet radius $R = 4\ \mu m$, normalized to the droplet concentration $500\ \text{cm}^{-3}$, which is a droplet spectrum typical of continental or polar stratus clouds [e.g., Curry, 1986]. This superposition, which could be measured by a sensitive particle counter, is shown in Figure 5. One can see that the full size spectrum of the particles in a liquid cloud combines the wet CCN inverse power law on the left and droplet spectrum (of gamma distribution type) on the right with maximum at 3-4 $\mu m$, causing the spectral gap. The most interesting feature of this spectra is that the gap is especially well pronounced at higher supersaturation, 0.1%, and is smoothed at lower $S = 0.01 - 0.005\%$.

A very sharp gap at $r = 0.05-0.5\ \mu m$ was obtained in the first numerical calculations of the regular condensation growth of droplet population by Morley [1959], while a much smoother gap has been measured in clouds (see review by Pruppacher and Klett [1997]). Junge [1963] hypothesized that this sharp gap can be smoothed by the variability of the critical supersaturation of CCN activation. Equation (38), being in agreement with Junge's hypotheses, provides a quantitative description for this effect. Figure 5 shows that the radius of the gap increases with increasing supersaturation; the minimum in the size spectrum lies about $r = 0.8\ \mu m$ at $S = 0.1\%$, more typical of vigorous updrafts in convective clouds, being very sharp, and is smoothed and displaced to $r = 2\ \mu m$ at $S < 0.01\%$, more typical of stratus clouds and fog. This feature of the combined (aerosol plus droplet) size spectra allows indirect estimations of the very small supersaturations in clouds which are very difficult to measure otherwise.

To clarify further the difference between wet aerosol and cloud drops, we consider the cloud condensation nuclei activity spectrum (Twomey [1959] law) which can be derived using this model. The value of a nucleus activity $A_b(S)$ which corresponds to the boundary point $r = r_b$ can be determined as the minimum in $r$ of the cubic parabola (18), where $S(r) = 0$ (condition of equilibrium). Differentiating (18) with respect to $r$ and using this equilibrium condition, we obtain, following Mason [1971]

$$A_b(S_a) = \frac{4M^3}{27 S_a^2} = \frac{B}{3} r_b^2 \tag{40}$$

The point in the activity spectrum (24), where $A = A_b(S_a)$, is the point where activation of CCN occurs if supersaturation increases (or deactivation of CCN if $S$ decreases).

In order to derive the CCN activity spectra $f_b(S_a)$ we can write, similarly to (22),

$$f_b(S_a) dS_a = f_A(A_b) dA_b \tag{41}$$

The minus sign occurs because the boundary value of $A_b(S_a)$ decreases with increasing supersaturation (or $r_b$ decreases; see (39) and Figure 5). That is, for larger values of supersaturation, the nuclei can still be in equilibrium at a smaller activity and the minimum at $r_b$ between the droplet and aerosol size spectra moves to the smaller radii. Substituting (40) into (41), we obtain, after some transformations,

$$f_b(S) = C_T S^K \tag{42}$$

where the coefficients are

$$C_T = 2N_r \mu^{-1} R \left( \frac{27b}{4B^3} \right) \tag{43}$$

$$K_T = \frac{\mu \beta}{1 + \beta} \tag{44}$$

The supersaturation activation spectrum of the form (42), considered by Twomey [1959], Leven and Sedanov [1966] and many others [see Pruppacher and Klett, 1977], can be very useful in cloud models, especially in those with explicit microphysics. The concentration of droplets activated within the supersaturation range ($0, S$) can be obtained by integration (42).

$$N = \int_0^S f(S) dS = C S^k \tag{45}$$

where $S$ is supersaturation expressed in % and

$$C = 10^{-7} \frac{27b}{4B^3} \frac{C_T}{K_T} = K_T + 1 = \frac{k-1}{1 + \beta} \tag{46}$$

The equations (42) and (45) have the form of the Twomey [1959] law.

Equations (44) and (46) relate explicitly the power indices $K_T$ and $k$ to the Junge index $\mu$ and parameter of soluble fraction $\beta$. These indices are also related to the humidity index $K$ from (34) and (44, 46) as

$$K_T = 2R - 1 \quad k = 2R \tag{47}$$

This expression allows determination of supersaturation activation spectrum from measurements of the humidity dependence of aerosol size spectra as described above or from the humidity dependence of optical parameters as described by Khvorostyanov and Curry [this issue].

The average values of $k$ presented by Pruppacher and Klett [1977] based on measurements obtained over the globe vary over the range $k = 0.3-1.4$, with larger values in maritime air masses and smaller values in continental air masses. Locally the measured values obtained in the Arctic during April 1992 by Hegg et al. [1995] varied from $k = 0.26-1.39$, with a mean value of $k = 0.71 \pm 0.29$. Detailed observations [e.g., Hudson, 1984] and calculations based on numerical methods using lognormal size distributions [e.g., Feingold et al., 1994] show that the value of $k$ itself depends on $S$; that is, $k$ decreases with increasing $S$ in such a way that $k > 1-1.5$ for $S \leq 0.1\%$ and $k < 0.3-0.5$ for $S \sim 1\%$.

These variations in $k$ can be interpreted using our model as follows. The inverse power law can serve as a good approximation to the real aerosol spectra because it follows from the rigorous theory of aerosol coagulation, but the slopes $\mu$ can vary for different parts of the size spectrum since $\mu$ depends on the prevailing mechanisms of aerosol formation. The rigorous solution to the coagulation equation gives the index $\mu = 2.5$ for $r \sim 1\ \mu m$, due to the combined effects of Brownian coagulation and sedimentation, and $\mu = 4.5$ for $r > 1\ \mu m$ due to prevailing sedimentation [see Pruppacher and Klett, 1977]. Near the modal radius, $r = 0.03-0.05\ \mu m, \mu = 0$. Thus the aerosol size spectrum can be approximated by a superposition of several inverse power law spectra, whose indices increase with radius as described above.
Table 3. Indices $k$ of Power Law (45) of CCN Supersaturation Activity Spectrum From (47) and Corresponding Boundary Radii $r_\omega$ (39) and Supersaturations $S$.

<table>
<thead>
<tr>
<th>Junge Index $\mu$</th>
<th>1.0</th>
<th>1.6</th>
<th>1.8</th>
<th>2.0</th>
<th>2.2</th>
<th>2.5</th>
<th>3.0</th>
<th>4.0</th>
<th>4.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta = 0$</td>
<td>0</td>
<td>0.6</td>
<td>0.8</td>
<td>1.0</td>
<td>1.2</td>
<td>1.5</td>
<td>2.0</td>
<td>3.0</td>
<td>3.5</td>
</tr>
<tr>
<td>$\beta = 0.5$</td>
<td>0</td>
<td>0.4</td>
<td>0.53</td>
<td>0.67</td>
<td>0.8</td>
<td>1.0</td>
<td>1.33</td>
<td>2.0</td>
<td>2.33</td>
</tr>
</tbody>
</table>

Boundary Radii $r_\omega$ (39) and Supersaturations $S$ Corresponding to the Above $\mu$ and $k$

<table>
<thead>
<tr>
<th>$r_\omega$, $\mu$m</th>
<th>$S_%$</th>
<th>$r_\omega$, $\mu$m</th>
<th>$S_%$</th>
<th>$r_\omega$, $\mu$m</th>
<th>$S_%$</th>
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<th>$S_%$</th>
<th>$r_\omega$, $\mu$m</th>
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</thead>
<tbody>
<tr>
<td>$r_\omega = 1$</td>
<td>0.08</td>
<td>$r_\omega = 1$</td>
<td>0.1</td>
<td>$r_\omega = 1$</td>
<td>0.6</td>
<td>$r_\omega = 1$</td>
<td>0.8</td>
<td>$r_\omega = 1$</td>
</tr>
</tbody>
</table>

The values of $k$ determined from (45) for various values of $\mu$ and $\beta$ are presented in Table 3. Also presented in this table are the values of the boundary radius $r_\omega$ and corresponding $S$ as defined by (39) (recall that $r_\omega$ is the lower boundary of activated nuclei). Table 3 shows that the values of $k$ are lower for $\beta = 0.5$ than for $\beta = 0$. For $\beta = 0.5$, $k = 1$ at $\mu = 2.5$, which corresponds to $r_\omega = 0.1$ um and $S = 0.8\%$. For values of $\mu > 2.5$ (corresponding to $r_\omega = 0.6$ 1 $\mu$m and $S = 0.08\%$ 0.13%), then $k > 1$. Note that supersaturations calculated with explicit microphysical models for stratuscumulus clouds [Feingold et al., 1994] did not exceed 0.4% and were typically of the order of 0.1% even with vertical velocities up to 0.5 m s$^{-1}$. Hence for values of $\mu \leq 0.1$% that are typical of stratuscumulus clouds, values of $k \leq 1.3$–2 are determined from the present model. For high values of supersaturation associated with $\mu < 2.5$ and $r_\omega < 0.1 \mu$m, lower values of $k \leq 0.5$–0.8 are obtained. These values of $k$ are in agreement with measured data and with calculations made by Feingold et al., [1994] who obtained slopes of $k \leq 0.2$–0.3 at $S \leq 1\%$ and $k > 1$ 1.5 at $S \leq 0.1\%$.

Note that the value $S \leq 1\%$ is a characteristic supersaturation used in the chambers when processing aerosol (CCN) probes in field experiments; however, values of supersaturation this high are rarely seen in atmospheric clouds. Hence use of low values of $k \leq 0.3$–0.6 obtained at high supersaturations may lead to underestimation of the nucleation rate and droplet concentrations in the cloud models that do not produce high $S$. This issue is of particular importance for cloud models with explicit microphysics [see Feingold et al., 1994; Khvorostyanov, 1995; Pruppacher and Klett, 1997].

The above consideration shows that the aerosol size spectra can be represented as a superposition of the several Junge power laws, and supersaturation activity spectra can be represented by a superposition of $2$–$4$ power laws with different indices of $k$, as

$$f(S) = \sum C_k S^k$$  

(48)

Each of the terms in the sum (48) corresponds to the different fractions in the aerosol size spectrum, with larger values of $k$, for larger size fraction with larger $\mu$ and smaller corresponding $S$ and with smaller values of $k$, for smaller sizes and larger $S$.

5. Conclusions

In this paper, we have derived simple yet accurate analytical formulas for calculation of the equilibrium aerosol radii and size spectra accounting for hygroscopic growth. The aerosol model described is based on the assumption that the dry aerosol obeys the Junge [1952] law, and then the aerosol properties are parameterized with use of the following three parameters: the Junge index of dry aerosol $\mu$, the amount of soluble fraction $\beta$, and total aerosol concentration $N$. These analytical expressions account explicitly for the different chemical compositions and microstructure of the dry aerosol.

It is shown that analytical expressions for the wet size spectra are different for three different humidity regimes: (1) moderate humidity, (2) high humidity but subsaturated, and (3) interstitial cloud aerosol under supersaturated conditions. The transition in aerosol size spectra between these humidity regimes is not smooth, but rather, the slopes of the size spectra change in a step-like manner during the following transitions: (1) from the Junge index $\mu$ of dry aerosol to the index $\mu_{\omega}$ of wet aerosol at deliquescence; (2) at $H \leq 0.97$, the slope of the size spectra changes to $\mu_{\omega}$, typically associated with an increase in the number of large particles; and (3) when supersaturation becomes positive and a cloud forms, the size spectra of interstitial aerosol are limited on the upper end, the upper limit depending on the supersaturation.

The equilibrium aerosol size spectra overlaps with the drop size spectrum. A gap occurs in the combined size spectra, located at $r \approx 0.4$–0.8 $\mu$m at high $S \geq 0.1$–0.2%, typical of convective clouds or vigorous updrafts, and $r \approx 2 \mu$m at low $S \approx 0.005$–0.01%, typical of stratified clouds or fog. The Twomey [1959] cloud condensation nuclei (CCN) power law is then derived from this aerosol model, and its parameters are analytically related to the aerosol microstructure.

Although this aerosol model is somewhat simplified, it reveals some internal relations among different aerosol properties. Since the model has been derived in the form of a power law, the power law exponents in the [Kasten, 1969; Hanel, 1972] law and Twomey [1959] law, previously determined empirically, can now be interpreted physically and specified in the context of physical parameters. This model can be a useful tool for many applications, for example, analysis of in situ and remote sensing measurements of the aerosol microphysical and optical properties, estimation of aerosol climatic effects, and in-cloud models and climate models for simple parameterization of aerosol microphysics and optics. This simple aerosol model can be generalized to account for more complicated polymodal aerosol size spectra by superposing several size spectra with appropriate values of $\mu$, $\beta$, and $N$ for each spectrum.

Application of this model to determination of aerosol optical properties is performed by Khvorostyanov and Curry [this
issue. In particular, the well-known empirical law for the attenuation coefficient wavelength dependence (Angstrom law) and the relative humidity dependence derived in this paper are related to each other and to aerosol microstructure.

Acknowledgments. This research was supported by the DOE ARM program and by the NASA FIRE Project. Olga Melnik is thanked for her help in programming and calculations, and Jody Norman and Olga Melnik are thanked for their assistance in preparation of the manuscript.

References


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(Received January 8, 1998; accepted July 29, 1998.)