Analysis of aerosol interactions with numerical techniques for solving coagulation, nucleation, condensation, dissolution, and reversible chemistry among multiple size distributions

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Received 28 December 2001; revised 11 March 2002; accepted 13 March 2002; published 2 October 2002.

This paper describes new and modified numerical techniques for solving the size- and time-dependent aerosol processes of nucleation, coagulation, condensation, dissolution, and reversible chemistry among multiple aerosol particle size distributions and the gas phase and over the entire relative humidity (RH) range. The techniques treat particle number, mole, and volume concentrations, solution and nonsolution densities, and refractive index consistently. Some findings include the following: (1) Coagulation internally mixes particles of different original composition over the entire size distribution. (2) Coagulation internally mixes a greater fraction of larger than smaller particles. (3) Coagulation internally mixes larger particles with more other distributions than it does smaller particles. (4) Coagulation among multiple distributions produces the same summed size distribution as coagulation of a single distribution when the sum of initial distributions is the same in both cases. (5) In a competition for vapor between homogeneous nucleation and condensation, the relative importance of condensation increases with an increasing number of background particles. (6) In the absence of a continuous source of new particles, coagulation, condensation, dissolution, hydration, and chemical reaction internally mix most particles within half a day under moderately polluted conditions. (7) Condensation increases the fractional coating of small more than large particles. (8) The real refractive index of a particle containing electrolytes is higher at low RHs than at high RHs. (9) The difference between total particle and solution real refractive indices increases with decreasing RH. (10) A solution real refractive index generally increases with decreasing particle size.

INDEX TERMS: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0360 Atmospheric Composition and Structure: Transmission and scattering of radiation; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 1610 Global Change: Atmosphere (0315, 0325); KEYWORDS: aerosols, coagulation, condensation, nucleation, equilibrium, internal mixtures


1. Introduction

Many studies to date have described numerical techniques for solving the differential coagulation equation [e.g., Lushnikov, 1975; Turco et al., 1979; Sack and Brock, 1979; Gelbard and Seinfeld, 1980; Tsang and Brock, 1982; Seigneur, 1982; Friedlander, 1983; Warren and Seinfeld, 1985; Tzivion et al., 1987; Toon et al., 1988; Strom et al., 1992; Kim and Seinfeld, 1992; Jacobson et al., 1994; Kostoglu and Karabelas, 1994; Jacobson and Turco, 1995; Binkowski and Shankar, 1995; Kumar and Ramkrishna, 1996; Fassi-Fihri et al., 1997; Russell and Seinfeld, 1998; Trautmann and Wanner, 1999; Fernandez-Diaz et al., 2000; Bott, 2000; Jeong and Choi, 2001; Sandu, 2002]. Many studies have also examined solutions to condensational growth equations [e.g., Mordy, 1959; Middleton and Brock, 1976; Gelbard and Seinfeld, 1980; Varoglu and Finn, 1980; Smolarkiewicz, 1983; Friedlander, 1983; Tsang and Brock, 1986; Whitby, 1985; Brock et al., 1986; Tsang and Korgaonkar, 1987; Toon et al., 1988; Rao and McMurry, 1989; Tsang and Huang, 1990; Gelbard, 1990; Pilinis, 1990; Kim and Seinfeld, 1990, 1992; Jacobson and Turco, 1995; Lister et al., 1995; Binkowski and Shankar, 1995; Jacobson, 1997c; Kleeman et al., 1997; Gelbard et al., 1998; Chock and Winkler, 2000; Nguyen and Dabdub, 2001; Sandu and Borden, 2001]. A third group of studies has examined solutions to equations for nonequilibrium dissolutional growth plus equilibrium reversible chemistry of electrolytes [Jacobson et al., 1996; Meng and Seinfeld,
imaginary refractive from compositions in multiple distributions are also given.

2. Particle Size Distributions

[6] The numerical treatments here assume that particles can be described by any number of size distributions, each with any number of size bins and any number of components within each size bin. Each size bin \( i \) in each size distribution \( N \) is characterized by a number concentration, \( n_{Ni} \) (number of particles per cubic centimeter of air). Each component \( q \) in each size bin of each distribution is characterized by a mole concentration, \( c_{q,Ni} \) (moles per cubic centimeter of air).

[7] For many processes, such as coagulation, single-particle volume information is needed. The calculation of single-particle volume takes into account the facts that particles contain a solution and nonsolution component and solution density varies as a function of electrolyte concentration. Single-particle volumes (cubic centimeters per particle) are calculated as

\[
v_{Ni} = \frac{v_N}{n_{Ni}}
\]

where \( v_{Ni} \) is the volume concentration (cubic centimeters of particle per cubic centimeter of air) of the total particle and is calculated as

\[
v_{Ni} = v_{s,NI} + \sum_{q=1}^{N_{NS}} v_{q,NI} = v_{s,NI} + \sum_{q=1}^{N_{NS}} \frac{m_{q}}{\rho_{q}} c_{q,NI}
\]
Sea spray – soil AB All except BC and OM – Co Sea spray – sulfate AD All except BC, OM, soil – Co Sea spray – BC AE All except OM and soil – Co Sea spray – OM AF All except BC and soil – Co Soil – sulfate BD All except BC, OM, and species with Na, Ca, Mg, K – Co Soil – BC BE All except OM, and species with Na, Ca, Mg, K – Co Soil – OM BF All except BC and species with Na, Ca, Mg, K – Co Sulfate – BC DE All except OM, soil, and species with Na, Ca, Mg, K – Co Sulfate – OM DF All except BC, soil, and species with Na, Ca, Mg, K – Co BC – OM EF All except soil, and species with Na, Ca, Mg, K – Co Internal mixture MX All – Co

<table>
<thead>
<tr>
<th>Distribution Name</th>
<th>Symbol</th>
<th>Potential Components</th>
<th>Initialized?</th>
<th>Sources of New Particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sea spray</td>
<td>A</td>
<td>All in (b) except BC, OM, and soil</td>
<td>Yes</td>
<td>Em*</td>
</tr>
<tr>
<td>Soil</td>
<td>B</td>
<td>All except BC, OM, and species with Na, Ca, Mg, K</td>
<td>Yes</td>
<td>Em</td>
</tr>
<tr>
<td>Sulfate</td>
<td>D</td>
<td>All except BC, OM, soil, and species with Na, Ca, Mg, K</td>
<td>Yes</td>
<td>Nucleation</td>
</tr>
<tr>
<td>BC with 0–5% shell</td>
<td>E1</td>
<td>All except OM, soil, and species with Na, Ca, Mg, K</td>
<td>Yes</td>
<td>Em</td>
</tr>
<tr>
<td>BC with 5–20% shell</td>
<td>E2</td>
<td>All except OM, soil, and species with Na, Ca, Mg, K</td>
<td>–</td>
<td>Gr from E1</td>
</tr>
<tr>
<td>BC with &gt;20% shell</td>
<td>E3</td>
<td>All except OM, soil, and species with Na, Ca, Mg, K</td>
<td>–</td>
<td>Gr from E1 and E2</td>
</tr>
<tr>
<td>OM</td>
<td>F</td>
<td>All except BC, soil, and species with Na, Ca, Mg, K</td>
<td>Yes</td>
<td>Em</td>
</tr>
<tr>
<td>Sea spray – soil</td>
<td>AB</td>
<td>All except BC and OM</td>
<td>–</td>
<td>Co</td>
</tr>
<tr>
<td>Sea spray – sulfate</td>
<td>AD</td>
<td>All except BC, OM, soil</td>
<td>–</td>
<td>Co</td>
</tr>
<tr>
<td>Sea spray – BC</td>
<td>AE</td>
<td>All except OM and soil</td>
<td>–</td>
<td>Co</td>
</tr>
<tr>
<td>Sea spray – OM</td>
<td>AF</td>
<td>All except BC and soil</td>
<td>–</td>
<td>Co</td>
</tr>
<tr>
<td>Soil – sulfate</td>
<td>BD</td>
<td>All except BC, OM, and species with Na, Ca, Mg, K</td>
<td>–</td>
<td>Co</td>
</tr>
<tr>
<td>Soil – BC</td>
<td>BE</td>
<td>All except OM, and species with Na, Ca, Mg, K</td>
<td>–</td>
<td>Co</td>
</tr>
<tr>
<td>Soil – OM</td>
<td>BF</td>
<td>All except BC and species with Na, Ca, Mg, K</td>
<td>–</td>
<td>Co</td>
</tr>
<tr>
<td>Sulfate – BC</td>
<td>DE</td>
<td>All except OM, soil, and species with Na, Ca, Mg, K</td>
<td>–</td>
<td>Co</td>
</tr>
<tr>
<td>Sulfate – OM</td>
<td>DF</td>
<td>All except BC, soil, and species with Na, Ca, Mg, K</td>
<td>–</td>
<td>Co</td>
</tr>
<tr>
<td>BC – OM</td>
<td>EF</td>
<td>All except soil, and species with Na, Ca, Mg, K</td>
<td>–</td>
<td>Co</td>
</tr>
<tr>
<td>Internal mixture</td>
<td>MX</td>
<td>All</td>
<td>–</td>
<td>Co</td>
</tr>
</tbody>
</table>

*N* is the number of electrolytes in the solution. In equation (5),

\[
\chi_{q,NI} = \frac{m_{q}c_{q,NI}}{m_{NI}}
\]

is the mass fraction of component *q* in solution and *p*a, *q*, *NI* is the mass density of electrolyte *q* as if it were alone in solution at the same weight percent as the current weight percent of total solute. Density polynomials for several electrolytes are available in the work of Tang [1997].

[9] The numerical methods described here assume that each distribution can be affected by nucleation, emissions, coagulation, condensation, dissolution, chemical equilibrium, transport, and removal (although emissions, transport, and removal are not simulated here). Table 1a shows a set of 18 size distributions used here for all the simulations discussed. Table 1b lists the components treated in each distribution of Table 1a, except as specified in Table 1a. For each distribution, 60 size bins, ranging from 0.001 to 120 μm in radius, are used. In sum, this study considers 32,400 concentrations in a single spatial grid cell (18 size distributions × an average of 30 species per distribution × 60 size bins per species per distribution).

[10] Table 1a identifies the sources of new particles in each distribution. For four distributions (A, B, E1, and F), the only source of new particles is emissions. For one distribution (D), the only source of new particles is homogenous nucleation. For 12 distributions (AB, AD, AE, AF, BD, BE, BF, DE, DF, EF, and MX), the only new-particle source is coagulation between simpler distributions. For two distributions (E2 and E3), the only new-particle source is condensation onto E1 or E2, respectively. Distributions E1, E2, and E3 contain black carbon (BC) with different volume fractional coatings (0–5%, 5–20%, and >20%, respectively). BC is emitted into (and initialized in) distribution E1. When the fractional coating of E1 particles in a size bin increases above 5%

<table>
<thead>
<tr>
<th>Species Formula</th>
<th>Species Formula</th>
<th>Species Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O(aq)</td>
<td>CO⁻</td>
<td>KHSO₄(s)</td>
</tr>
<tr>
<td>H₂CO₃(aq)</td>
<td>NH₄NO₃(s)</td>
<td>K₂SO₄(s)</td>
</tr>
<tr>
<td>H₂SO₄(aq)</td>
<td>NH₄Cl(s)</td>
<td>K₂CO₃(s)</td>
</tr>
<tr>
<td>H⁺</td>
<td>NH₄H₂SO₄(s)</td>
<td>Ca(NO₃)₂(s)</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>(NH₄)₂SO₄(s)</td>
<td>Ca(NO₃)₂(s)</td>
</tr>
<tr>
<td>Na⁺</td>
<td>(NH₄)₂H₂SO₄(s)</td>
<td>CaSO₄(s)</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>(NH₄)₂CO₃(s)</td>
<td>CaCO₃(s)</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>NaNO₃(s)</td>
<td>Mg(NO₃)₂(s)</td>
</tr>
<tr>
<td>K⁺</td>
<td>NaCl(s)</td>
<td>MgCl₂(s)</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>NaH₂SO₄(s)</td>
<td>MgSO₄(s)</td>
</tr>
<tr>
<td>SO₂</td>
<td>Na₂SO₄(s)</td>
<td>MgSO₄(s)</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>Na₂CO₃(s)</td>
<td>Soil</td>
</tr>
<tr>
<td>CI⁻</td>
<td>KNO₃(s)</td>
<td>BC</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>KCl(s)</td>
<td>OM</td>
</tr>
</tbody>
</table>

*Em = emissions, Nuc = homogeneous nucleation, Co = coagulation, Gr = condensational and/or dissolutional growth. All distributions are affected by self-coagulation loss to larger sizes and heterocoagulation loss to other distributions (except the MX distribution, which has no heterocoagulation loss). In addition, particles in all distributions can grow in size by condensation and dissolution, reversible equilibrium chemistry, and equilibrium hydration. The difference between distributions A and AD is that the only source of new A particles is emissions, whereas that of new AD particles is coagulation of A with D, A with AD, or D with AD particles. The differences among distributions E1, E2, E3, and DE are that the only source of new E1 particles is emissions, the only sources of E2 and E3 particles are growth from E1 and E2, respectively, and the only source of new DE particles is coagulation of E1, E2, or E3 with D or DE and coagulation of D with DE. Each size distribution contains multiple size bins.*

[11] Each size bin in each size distribution is characterized by a high- and low-edge volume, which equal a constant, *V*_µ₉, multiplied by the high- and low-edge volume, respectively, of the next-smallest bin. One way to initialize the high- and low-edge volume of a bin is given by Jacobson [1999a, equations (14.6) and (14.7)]. Other ways are also possible. All particles in the bin, though, have a single characteristic volume ( *υ*N) between the low- and high-edge volumes of the bin. This single volume can change as the particles grow, evaporate, coagulate, etc. If...
the volume increases above the high-edge volume of the bin, all particles in the bin are moved to and averaged with particles in the next-largest bin. This size bin structure is the moving-center structure [Jacobson, 1997a, 1999a, pp. 420–4201]. Results from it have been compared with other size structures by Jacobson [1997a] and Zhang et al. [1999] and are compared further here with those from another structure, the full-moving structure.

3. Coagulation

[12] The coagulation scheme described here is an extension of an earlier volume-conserving, noniterative, unconditionally stable coagulation scheme in which multiple size distributions were considered [Jacobson et al., 1994]. When external mixtures coagulated in the original scheme, they were sent into a single internally mixed distribution. For this work, the scheme was modified to treat coagulation into and among any number of externally mixed, binary, ternary, etc. combinations of distributions and any number of components in each distribution (maintaining volume conservation). In the work of Jacobson et al. [1994], results from the scheme were compared with analytical and numerical solutions for one distribution. There are no analytical solutions available for multiple distributions, but it can be shown mathematically and from numerical simulations that coagulation within and among multiple distributions gives the same solution, summed over all distributions, as coagulation within one distribution if the initial volume concentrations, summed over all distributions, are the same in both cases. As such, the accuracy of the multiple-distribution solution is exactly the same as the single-distribution solution. Coagulation rate coefficients treated here include those for Brownian motion, Brownian diffusion enhancement, gravitational collection, turbulent inertial motion, and turbulent shear [e.g., Jacobson, 1999a, Figure 16.4 and equations (16.28)–(16.34)].

[13] The volume-conserving solution to coagulation among any number of size distributions, size bins in each distribution, and component in each distribution is given as follows. The final number concentration of particles in bin $k$ of distribution $N$ at time $t$ is

$$n_{Nk,t} = n_{Nk,t-h} + h(T_1 + T_2)\left[1 + hT_3\right]$$

\[T_1 = \frac{1}{v_{Nk,t-h}} \sum_{M=1}^{N_N} \left[ P_{N,M} \sum_{j=1}^{k} \left( \alpha_{N,M}^{Nk,t-k} \frac{n_{Nk,t-k}}{v_{Nk,t-k}} \right) n_{M,j} \right] \]

\[T_2 = \frac{1}{v_{Nk,t-h}} \sum_{M=1}^{N_N} \sum_{j=1}^{k} \left( Q_{M,N} \sum_{i=1}^{j-1} \alpha_{M,i}^{Nk,t-i} n_{M,i} \right) n_{Nk,t-k} \]

\[T_3 = \sum_{j=1}^{N_N} \left( 1 - \frac{v_{Nk,t-h} + h(T_1 + T_2)}{1 + hT_3} \right) \frac{n_{Nk,t-k}}{v_{Nk,t-k}} \left( 1 - \frac{v_{Nk,t-h} + h(T_1 + T_2)}{1 + hT_3} \right) n_{M,j} \]

where $h$ is the time step size, $t - h$ indicates a value at the beginning of the time step, $N_N$ is the total number of size distributions (18 in Tables 1a and 1b), $N_N$ is the number of size bins in each distribution, $\alpha_{N,M}^{Nk,t-k}$ is the coagulation rate coefficient (cubic centimeters per particle per second) between a particle in size bin $i$ of distribution $N$ and a particle in bin $j$ of distribution $M$, and $f_{N,M,j,k}^{Nk,t-k}$ is the fraction of the summed single-particle volume $V_{N,M,j,k}^{Nk,t-k} = v_{N,M,j,k}^{Nk,t-k} + v_{N,M,j,k}^{Nk,t-k}$ partitioned into bin $k$ of distribution $N$ at the beginning of the time step. This formulation allows the average single-particle volume ($v$) of a particle in a size bin to change each time step, which is necessary for the moving-center size structure, in which the single-particle volume in a bin can vary between the low- and high-edge volume in the bin. For a size bin structure in which single-particle volume does not change in time (e.g., a stationary structure), the volume fractions are calculated only once, at the beginning of the simulation. In either case, volume fractions are calculated as

$$f_{N,M,j,k}^{Nk,t-k} = \begin{cases} \frac{v_{N,M,j,k}^{Nk,t-k} + v_{N,M,j,k}^{Nk,t-k}}{v_{N,M,j,k}^{Nk,t-k}} & k < N_N \\ 1 - f_{N,M,j,k}^{Nk,t-k} & k > 1 \\ 1 & k = N_N \\ 0 & \text{all other cases} \end{cases}$$

\[ (8) \]

[14] Finally, $P$, $Q$, and $L$ in equation (7) are either 1 or 0, depending on the coagulation interactions accounted for. The values are illustrated by considering Table 2, which identifies a possible set of coagulation interactions among the distributions in Tables 1a and 1b. The parameter $P_{N,M} = 1$ if particles in distribution $N$ coagulating with particles in distribution $M$ produce larger particles in distribution $N$. For example, sea spray–soil (AB) plus sea spray (A) produces more sea spray–soil (AB); thus, $P_{AB,A} = 1$. The parameter $Q_{M,N} = 1$ if particles in distribution $I$ coagulating with particles in distribution $M$ produce particles in distribution $N$, where $I \neq M$ and $I \neq N$. For example, soil (B) plus sulfate (D) produces soil–sulfate (BD); thus, $Q_{BD,B} = 1$. The parameter $L_{N,M} = 1$ if particles in distribution $N$ coagulating with particles in distribution $M$ do not produce particles in distribution $N$. For example, soil (B) plus sulfate (D) does not produce soil (B); thus, $L_{BD,D} = 1$. On the other hand, soil–sulfate (BD) plus sulfate (D) produces soil–sulfate (BD); thus, $L_{BD,D} = 1$ in that case.

[15] In equation (7), term $T_1$ accounts for production into distribution $N$ due to self-coagulation (e.g., $N + N$) and heterocoagulation of $N$ with a simpler distribution $M$. Term $T_2$ accounts for production into distribution $N$ due to heterocoagulation of two independent distributions, $I$ and $M$. The first part of term $T_2$ accounts for both self-coagulation loss ($N + N$) and heterocoagulation loss ($N + M$) to larger sizes of the same distribution ($N$). The second part of $T_3$ accounts for heterocoagulation loss ($N + M$) to any distribution aside from $N$.

[16] Volume concentrations of each individual component $q$ in size bin $k$ of distribution $N$ are similarly solved with

$$v_{q,Nk,t} = \frac{v_{q,Nk,t-h} + h(T_1 + T_2)}{1 + hT_3}$$
Table 2. Coagulation Interactions

<table>
<thead>
<tr>
<th>Size Distribution Name</th>
<th>Symbol</th>
<th>Symbol of Second Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>Sea spray</td>
<td>A</td>
<td>AB</td>
</tr>
<tr>
<td>Sulfate</td>
<td>D</td>
<td>AD</td>
</tr>
<tr>
<td>BC with 0–5% shell</td>
<td>E1</td>
<td>AE</td>
</tr>
<tr>
<td>BC with 5–20% shell</td>
<td>E2</td>
<td>AE</td>
</tr>
<tr>
<td>BC with &gt;20% shell</td>
<td>E3</td>
<td>AE</td>
</tr>
<tr>
<td>OM</td>
<td>F</td>
<td>AF</td>
</tr>
<tr>
<td>Sea spray–soil</td>
<td>AB</td>
<td>AB</td>
</tr>
<tr>
<td>Sea spray–OM</td>
<td>AD</td>
<td>AD</td>
</tr>
<tr>
<td>Soil–AS</td>
<td>AE</td>
<td>AE</td>
</tr>
<tr>
<td>Soil–BC</td>
<td>AF</td>
<td>AF</td>
</tr>
<tr>
<td>Soil–OM</td>
<td>BD</td>
<td>BD</td>
</tr>
<tr>
<td>Sulfate–BC</td>
<td>BE</td>
<td>BE</td>
</tr>
<tr>
<td>Sulfate–OM</td>
<td>BF</td>
<td>BF</td>
</tr>
<tr>
<td>Internal mixture</td>
<td>EF</td>
<td>EF</td>
</tr>
</tbody>
</table>

The table gives the symbol of the size distribution into which two particles from either the same or different distributions coagulate to. For example, when a sea spray particle (A) coagulates with a soil particle (B), the resulting particle is a sea spray–soil (AB) particle. When three or more externally mixed (A...F) distributions or an externally mixed and binary (AB...EF) distribution or two binary distributions combine, they enter the mixed (MX) distribution. Thus, the combination of OM (F) with sea spray–soil (AB) gives a mixed particle (MX).
The scheme simultaneously solves binary or homomolecular dissolution of volatile species in the presence of solids. Condensation of involatile species [e.g., S(VI)] and for dissolution of volatile species in the presence of solids. The scheme simultaneously solves binary or homomolecular homogeneous nucleation, allowing growth and nucleation to compete for limited amounts of vapor.

[25] Although the APNCD scheme, itself, is noniterative, it relies on solubility and saturation vapor pressure terms calculated from an iterative equilibrium code. The chemical equilibrium code used is EQUISSOLV II [Jacobson, 1999b]. The equilibrium code iterates temperature-dependent equilibrium, solute activity coefficient, and water activity coefficient equations among sodium, chloride, potassium, calcium, magnesium, sulfate, nitrate, chloride, and carbonate substances in the ionic, liquid, and/or solid phases from 0.1 to 99.5% relative humidity (RH).

[21] EQUISSOLV II is used to calculate internal aerosol composition and LWC for use in saturation vapor pressure and solubility terms in the APNCD scheme. After the growth calculation, EQUISSOLV II is used a second time to equilibrate gas-phase NH₃ with all ions and solids in all size bins of the aerosol phase to determine final aerosol composition for the time step. The reason for equilibrating, instead of growing, NH₃ is that growth of S(VI), HNO₃, and HCl results in the production of anions in solution. The simultaneous growth of NH₃ leads to a charge imbalance that needs to be rectified either by adding H⁺, reducing NH₃ arbitrarily, or increasing another anion arbitrarily. Such arbitrary changes result in unreasonable aerosol compositions. Instead of balancing charge arbitrarily, gas-phase NH₃ is equilibrated with all size bins of the aerosol-phase simultaneously. This equilibration leads to exact charge balance in each bin and mass conservation of NH₃ between the gas phase and all aerosol size bins of all distributions. The equilibrium numerical solution of NH₃ between the gas phase and multiple size bins of the aerosol phase is unique in all cases, since only one gas is equilibrated. If two gases were equilibrated, the solution would not be unique when solids containing those gases were formed. The equilibration of gaseous NH₃ with the aerosol phase is, in effect, a time-dependent growth process because the amount of ammonium in the aerosol particles at a given time is tied to the growth rates of nitrate and chloride. The slower the growth rate of nitrate or chloride, the lesser the uptake of ammonium. The equilibrium treatment of NH₃ is also supported in part by Fridlind and Jacobson [2000] who found that, over the ocean, NH₃ be closer than HNO₃ to equilibration with coarse-mode particles.

[22] The APNCD scheme is derived by considering the following ordinary differential equations for condensation and dissolution, respectively, from the work of Jacobson [1997c]:

\[
\frac{\text{d}q_{N_i,j}}{\text{d}t} = k_{q_{N_i,j}} \left( C_{q_j} - S_{q_{N_i,j}} \left( C_{q_j} - S_{q_{N_i,j}} \right) \right)
\]  

Here the APC and APD schemes were combined and modified to form a noniterative, unconditionally stable scheme for solving nucleation, condensation, and dissolution simultaneously between the gas phase and multiple size distributions. The schemes were also modified to treat solids in some size bins and the absence of solids in others. The revised technique is the APNCD (Analytical Predictor of Nucleation, Condensation, and Dissolution) scheme. The technique simplifies to the APD scheme for dissolution in size bins in which no solids form and to the APC scheme for condensation of involatile species [e.g., S(VI)] and for dissolution of volatile species in the presence of solids.
In these equations, \( c_{q,N_i,t} \) is the mole concentration (mol cm\(^{-3}\)) of particle component \( q \) in size bin \( i \) of distribution \( N \). \( C_{q,t} \) is the gas-phase mole concentration (mol cm\(^{-3}\)) of component \( q \). \( C_{q,t} \) is the saturation vapor mole concentration (mol cm\(^{-3}\)) of component \( q \) over the surface of particles in size bin \( i \) of distribution \( N \), determined at the beginning of a time step, \( S_{q,N_i,t} \) is the saturation ratio at equilibrium [Jacobson, 1999a, equation (17.45)], which accounts for the Kelvin effect, \( k_{q,N_i,t-h} \) is the mass transfer rate \((\text{s}^{-1})\) of gas to the surface of particles in size bin \( i \), distribution \( N \) [Jacobson, 1999a, equation (17.62)], and \( H'_{q,N_i,t-h} \) is a dimensionless effective Henry’s constant for the size bin and distribution. For HNO\(_3\) dissolving in solution,

\[
H'_{\text{HNO}_3},Ni = R^* T \left( \frac{m_{c,c,Ni}}{1000} \right)^2 \frac{K_{\text{w,HNO}_3}}{c_{H^+},N_i t_{H^+/\text{NO}_3^-}}
\]

where \( R^* \) is the universal gas constant \((82.06 \text{ cm}^3 \text{ atm mol}^{-1} \text{ K}^{-1})\), \( T \) is Kelvin temperature, \( K_{\text{w,HNO}_3} \) is the equilibrium constant \((\text{mol}^2 \text{ kg}^{-2} \text{ atm}^{-1})\) of the reaction HNO\(_3\)(g) \( \rightleftharpoons \) H\(^+\) + NO\(_3^-\), and \( \gamma Ni \), H\(^+\)/NO\(_3^-\) is the dimensionless mixed activity coefficient of the ion pair H\(^+\)/NO\(_3^-\), determined from an equilibrium calculation. A similar expression can be written for HCl dissolving in solution. Integrating equations (10) and (11) individually for one size bin over a time step \( h \) gives

\[
c_{q,N_i,t} = c_{q,N_i,t-h} + h k_{q,N_i,t-h} \left( C_{q,t} - S_{q,N_i,t-h} C_{q,N_i,t-h} \right) \]

\[
c_{q,N_i,t} = H'_{q,N_i,t-h} C_{q,t} + \left( c_{q,N_i,t-h} - \frac{H'_{q,N_i,t-h} c_{q,t}}{S'_{q,N_i,t-h}} \right) \exp \left( -\frac{h S'_{q,N_i,t-h} k_{q,N_i,t-h}}{H'_{q,N_i,t-h}} \right)
\]

respectively, where the final gas mole concentration both cases, \( C_{q,t} \), is currently unknown. Final aerosol and gas concentrations are constrained by the gas–aerosol mass balance equation,

\[
C_{q,t} + \sum_{N=1}^{N_T} \sum_{i=1}^{N_B} c_{q,N_i,t} = C_{q,t-h} + \sum_{N=1}^{N_T} \sum_{i=1}^{N_B} c_{q,N_i,t-h}
\]

Substituting equations (13) and (14) into equation (15) and solving for \( C_{q,t} \) gives a generalized solution for both condensation and dissolution,

\[
C_{q,t} = \frac{\sum_{N=1}^{N_T} \sum_{i=1}^{N_B} \left( (1-D_{Ni}) k_{q,N_i,t-h} S'_{q,N_i,t-h} C_{q,N_i,t-h} + D_{Ni} c_{q,N_i,t-h} \left[ 1 - \exp \left( \frac{h S'_{q,N_i,t-h} k_{q,N_i,t-h}}{H'_{q,N_i,t-h}} \right) \right] \right)}{1 + h \sum_{N=1}^{N_T} \sum_{i=1}^{N_B} \left[ (1-D_{Ni}) k_{q,N_i,t-h} + D_{Ni} \left( \frac{S'_{q,N_i,t-h}}{S'_{q,N_i,t-h}} \right) \left[ 1 - \exp \left( \frac{h S'_{q,N_i,t-h} k_{q,N_i,t-h}}{H'_{q,N_i,t-h}} \right) \right] \right]}
\]

where \( D_{Ni} = 1 \) for dissolution and 0 for condensation in the bin of the distribution. In the current application, condensation is assumed to occur for H\(_2\)O growth onto cloud drops (if the RH > 100%) and for (SVI) growth at all RHs. (At RHs < 100%, H\(_2\)O growth is by equilibrium hydration). Condensation also occurs for HNO\(_3\) and HCl in size bins where a solid containing nitrate or chloride, respectively, forms. Solids containing nitrate include NH\(_4\)NO\(_3\), NaNO\(_3\), KNO\(_3\), Ca(NO\(_3\))\(_2\), and Mg(NO\(_3\))\(_2\). Solids containing chloride include NH\(_4\)Cl, NaCl, KCl, CaCl\(_2\), and MgCl\(_2\). Dissolution occurs for HNO\(_3\) and HCl over any size bin in which no solid containing nitrate or chloride, respectively, forms.

[21] Once equation (16) is solved for condensation, it is limited by \( C_{q,t} = \min(C_{q,t},C_{q,t-h}) \), since the explicit condensation term equation (16) can result in gas concentrations in excess of the maximum gas in the system. Equation (16) cannot fall below zero in any situation, and the limit is not needed if only dissolution is considered. \( C_{q,t} \) is then substituted back into equations (13) and (14) to give the final aerosol concentrations in size bins in which condensation and dissolution, respectively, occur. Whereas the dissolution solution (equation (14)) cannot result in aerosol concentrations \(<0\) or \(>C_{tot}\), the condensation solution (equation (13)) can. To remedy this, two limits are placed sequentially, after equations (13) and (14) are solved, when \( D_{Ni} = 0 \). The first is, \( c_{q,N_i,t} = \max(c_{q,N_i,t-h},0) \). The second, which applies only when \( c_{q,N_i,t} > c_{q,N_i,t-h} \) (and \( D_{Ni} = 0 \)), is

\[
C_{q,N_i,t} = \left\{ \begin{array}{ll}
C_{q,t-h} - C_{q,t} + \frac{\sum_{N=1}^{N_T} \sum_{i=1}^{N_B} \left( 1 - D_{Ni} \right)}{C_{q,t-h} - C_{q,t-h}} \max(c_{q,N_i,t-h},0) + D_{Ni} \max(c_{q,N_i,t-h},0) \\
\end{array} \right.
\]

where the \( c_{q,N_i,t} \) values on the right side of the equation are determined from equations (13) and (14). Equation (17) states that, when condensation occurs onto a particle, its concentration is set to the net loss in vapor due to condensation plus dissolution \((C_{q,t-h} - C_{q,t})\) plus the vapor gained by evaporation (from the condensation equation) minus the net change in vapor due to evaporation minus dissolution, all scaled by the rate of condensation in the bin (which equals \( c_{q,N_i,t} - c_{q,N_i,t-h} \) from equation (13)) divided by the sum of the rates of condensation into all bins in which condensation occurs. No limit is needed if only dissolution is considered. Thus, the solution scheme in equations (13)–(17) is exactly mass conserving between the gas and aerosol phases under all conditions and is noniterative. The solution scheme is also unconditionally stable because the difference between the numerical and exact solution is bounded between 0 and \( C_{tot} \), regardless of the time step or integration time.

[24] When HNO\(_3\) or HCl grows onto a size bin and a solid exists in the bin, condensational growth terms are needed in equations (13)–(17). Such terms require a saturation vapor mole concentration. For HNO\(_3\), the SPMC is calculated as
c_{\text{HNO}_3},S = \min
\left\{ \begin{array}{l}
\left( \frac{1000}{\text{H}_2\text{O}} \right)^2 \frac{c_{\text{H}^+,\text{NO}_3^-}}{m_{\text{c},\text{H}_2\text{O}}} \\
\left( \frac{1000}{\text{H}_2\text{O}} \right)^2 c_{\text{H}^+,\text{NO}_3^-} \\
\left( \frac{1000}{\text{H}_2\text{O}} \right)^2 c_{\text{H}^+,\text{NO}_3^-} \\
\left( \frac{1000}{\text{H}_2\text{O}} \right)^2 c_{\text{H}^+,\text{NO}_3^-} \\
\left( \frac{1000}{\text{H}_2\text{O}} \right)^2 c_{\text{H}^+,\text{NO}_3^-} \\
\end{array} \right.
\right. (18)

\text{HNO}_3(g) = \text{H}^+ + \text{NO}_3^-
(19)

which has the equilibrium coefficient expression,
\left( \frac{1000}{m_{\text{c},\text{H}_2\text{O}}} \right)^2 \frac{c_{\text{H}^+,\text{NO}_3^-}}{C_{\text{HNO}_3},S} = K_{\text{eq,HNO}_3} \left( \frac{\text{mol}^2}{\text{kg}^2 \cdot \text{atm}} \right)
(20)

Solving equation (20) for \( C_{\text{HNO}_3,S} \) gives the SVMC term in equation (18). The second process is the solid–gas reaction
\text{NH}_4\text{NO}_3(s) = \text{NH}_3(g) + \text{HNO}_3(g)
(21)

which has an equilibrium coefficient expression,
\left( \frac{R^*}{T} \right)^2 \frac{c_{\text{NH}_3,\text{HNO}_3}}{C_{\text{HNO}_3},S} = K_{\text{eq,NH}_3\text{NO}_3} \left( \text{atm}^2 \right)
(22)

All remaining processes are solid–ion reactions coupled with the gas–ion reaction \( \text{HNO}_3(g) = \text{H}^+ + \text{NO}_3^- \). The five solid–ion reactions are
\begin{align*}
\text{NH}_4\text{NO}_3(s) &= \text{NH}_4^+ + \text{NO}_3^- \\
\text{NaNO}_3(s) &= \text{Na}^+ + \text{NO}_3^- \\
\text{KNO}_3(s) &= \text{K}^+ + \text{NO}_3^- \\
\text{Ca(NO}_3)_2(s) &= \text{Ca}^{2+} + 2\text{NO}_3^- \\
\end{align*}
(23-26)

\text{Mg(NO}_3)_2(s) = \text{Mg}^{2+} + 2\text{NO}_3^-
(27)

The corresponding equilibrium coefficient expressions for these reactions are
\begin{align*}
\left( \frac{1000}{m_{\text{c},\text{H}_2\text{O}}} \right)^2 c_{\text{NH}_3,\text{HNO}_3} &= K_{\text{eq,NH}_3\text{NO}_3} \left( \frac{\text{mol}^2}{\text{kg}^2} \right) \\
\left( \frac{1000}{m_{\text{c},\text{H}_2\text{O}}} \right)^2 c_{\text{NaNO}_3} &= K_{\text{eq,NaNO}_3} \left( \frac{\text{mol}^2}{\text{kg}^2} \right) \\
\left( \frac{1000}{m_{\text{c},\text{H}_2\text{O}}} \right)^2 c_{\text{KNO}_3} &= K_{\text{eq,KNO}_3} \left( \frac{\text{mol}^2}{\text{kg}^2} \right) \\
\left( \frac{1000}{m_{\text{c},\text{H}_2\text{O}}} \right)^3 c_{\text{Ca(NO}_3)_2} &= K_{\text{eq,Ca(NO}_3)_2} \left( \frac{\text{mol}^1}{\text{kg}^3} \right) \\
\left( \frac{1000}{m_{\text{c},\text{H}_2\text{O}}} \right)^3 c_{\text{Mg(NO}_3)_2} &= K_{\text{eq,Mg(NO}_3)_2} \left( \frac{\text{mol}^1}{\text{kg}^3} \right)
\end{align*}
(28-32)

respectively. Coupling these equations with equation (20) and solving for \( C_{\text{HNO}_3,S} \) gives the SVMC terms in equation (18). The SVMCs for HCl are calculated in a similar way.

When homogeneous nucleation is coupled with growth, such as in the case of binary homogeneous nucleation/condensation of S(VI), the nucleation rate is first converted to a mass transfer rate between the gas and aerosol and added to the growth mass transfer rate in the first size bin. For example, if the binary homogeneous nucleation rate of S(VI)–water particles is \( R_{\text{S(VI)}-\text{H}_2\text{O}} \), the nucleation rate is first converted to a gas-phase mass transfer rate for nucleation (s\(^{-1}\)) with
\begin{align*}
R_{\text{S(VI)}-\text{H}_2\text{O}} \cdot \text{water particles} &= R_{\text{S(VI)}-\text{H}_2\text{O}} \\
\frac{\rho_{\text{S(VI)}} \cdot V_{\text{S(VI)}} \cdot F_{\text{S(VI)}}}{m_{\text{S(VI)}}} \\
\end{align*}
(33)

where \( \rho_{\text{S(VI)}} \) is the density of pure S(VI) (g cm\(^{-3}\)), \( V_{\text{S(VI)}} \) is the single-particle volume of a nucleated particle (cubic centimeters per particle), \( F_{\text{S(VI)}} \) is the volume fraction of S(VI) in an S(VI)–H\(_2\)O nucleated mixture, and \( m_{\text{S(VI)}} \) is the molecular weight (grams per mole) of S(VI). The denominator on the right side of equation (33) is the maximum gas
available for nucleation at the beginning of the time step (mol cm$^{-3}$). The mass transfer rate in equation (33) is then added to the growth mass transfer rate ($k_{S(VI)}$) for the size bin in which nucleated particles are placed (assumed to be bin $1$ in this equation), to give a total mass transfer rate to this bin of $k_{S(VI),N_{1,t}} = k_{S(VI),N_{1,t}} + k_{S(VI),N_{1,t}}$.

[26] After equations (13)–(17) are solved with the revised growth plus nucleation transfer rate, the new number concentration of S(VI)–H$_2$O particles due to homogeneous nucleation is calculated from the incremental change in mole concentration of S(VI) with

$$n_{S(VI),t} = n_{S(VI),t-1} + \text{MAX}\left[\left(c_{S(VI),t} - n_{S(VI),t-1}\right) \frac{m_{S(VI)}}{\rho_{S(VI)} N_{S(VI)}}, 0\right]$$

(34)

Once new particles are added, water, with a volume fraction of $1 - F_{S(VI)}$, is added to ensure the total volume added to the size distribution is consistent with the number of particles added to the distribution. This water content and the single-particle volume are adjusted subsequently when equilibrium hydration equations are solved.

[27] The advantage of coupling nucleation with growth is that rates for both are fast, and if these processes are operator split, one process will be favored extensively over the other. Solving both processes together allows for a more realistic competition among size bins for the limited amount of sulfuric acid gas available for nucleation and condensation.

[28] The nucleation rate, $R_{S(VI)}$, is calculated with classical theory in the simulations discussed below but could also be calculated with a parameterization. Zhang et al. [1999] compare several parameterizations of nucleation rates.

5. Aerosol Optical Properties

[29] Aerosol optical depths, single-scattering albedos, and asymmetry parameters are determined from particle scattering, absorption, and forward-scattering efficiencies from Mie theory calculations under the assumption that when a particle contains BC, BC is core material and all other material is shell material. Shell real and imaginary refractive indices for a given particle size and wavelength are obtained by first calculating solution and nonsolution refractive indices of all non-BC substances in the shell, then volume averaging the solution and nonsolution refractive indices to obtain average shell refractive indices. These refractive indices are then used in a core-shell Mie theory calculation in which BC is core [e.g., Toon and Ackerman, 1981].

[30] The volume-averaged shell real and imaginary refractive indices for a given wavelength $\lambda$ and particle size $i$ in distribution $N$ are calculated as

$$n_{\text{shell},i,\lambda} = \left(\frac{\sum_{q=1}^{N_q} q_{q,i} n_{q,i,\lambda}}{\sum_{q=1}^{N_q} q_{q,i}}\right) / \left(\frac{\sum_{q=1}^{N_q} q_{q,i} n_{q,i}}{\sum_{q=1}^{N_q} q_{q,i}}\right)$$

(35)

$$\kappa_{\text{shell},i,\lambda} = \left(\frac{\sum_{q=1}^{N_q} q_{q,i} \kappa_{q,i,\lambda}}{\sum_{q=1}^{N_q} q_{q,i}}\right) / \left(\frac{\sum_{q=1}^{N_q} q_{q,i} \kappa_{q,i}}{\sum_{q=1}^{N_q} q_{q,i}}\right)$$

(36)

where $n_{q,i,\lambda}$ and $\kappa_{q,i,\lambda}$ are the overall solution and individual component nonsolution real refractive indices, respectively, and $n_{q,i,\lambda}$ and $\kappa_{q,i,\lambda}$ are overall solution and individual component nonsolution imaginary refractive indices. The solution real refractive index is

$$n_{\text{s},i,\lambda} = \left(\frac{\sum_{q=1}^{N_q} q_{q,i} n_{q,i}}{\sum_{q=1}^{N_q} q_{q,i}}\right) / \left(\frac{\sum_{q=1}^{N_q} q_{q,i}}{\sum_{q=1}^{N_q} q_{q,i}}\right)$$

(37)

derived from equation (1) of Stelson [1990], where

$$R_{\text{s},i,\lambda} = R_{\text{H}_2\text{O},\lambda} + \sum_{q=1}^{N_q} R_{q,\lambda} q_{q,i}$$

(38)

is the product of the molar refraction ($R_{\text{s},i,\lambda}$, cm$^3$ mol$^{-1}$) and mole concentration ($c_{\text{s},i,\lambda}$, mol cm$^{-3}$) of the solution, and $R_{q,\lambda}$ is the partial molar refraction (cm$^3$ mol$^{-1}$) of individual solution component $q$ (either ion or electrolyte). Partial molar refractions are given for several ions and aqueous electrolytes in the works of Stelson [1990] and Tast [1997] at 550 nm. When data are not available, such as at solar- and thermal-IR wavelengths and for certain species, partial molar refractions for aqueous electrolytes are estimated by combining all ions in solution into hypothetical aqueous electrolytes, assuming the refractive index of the aqueous electrolyte equals that of the corresponding solid electrolyte, and applying the equation,

$$R_{q,\lambda} = \frac{m_q}{\rho_q} \left(\frac{n_{q,i}^2 - 1}{n_{q,i}^2 + 2}\right)$$

(39)

where $\rho_q$ is the real refractive index, $m_q$ is the molecular weight (g mol$^{-1}$), and $\rho_q$ is the density (g cm$^{-3}$) of the solid electrolyte. The assumption that the partial molar refraction of an aqueous electrolyte is similar to that of the corresponding solid electrolyte is substantiated by the work of Stelson [1990, Figure 1].

[31] The solution imaginary refractive index is estimated here with

$$\kappa_{\text{s},i,\lambda} = \frac{A_{\text{s},i,\lambda} c_{\text{s},i,\lambda}}{\rho_{\text{s},\lambda}}$$

(40)

where

$$A_{\text{s},i,\lambda} c_{\text{s},i,\lambda} = A_{\text{H}_2\text{O},\lambda} c_{\text{H}_2\text{O},\lambda} + \sum_{q=1}^{N_q} A_{q,\lambda} q_{q,i}$$

(41)

is the product of the molar absorption ($A_{\text{s},i,\lambda}$, cm$^3$ mol$^{-1}$) and the mole concentration of the solution, and $A_{q,\lambda}$ is the partial molar absorption (cm$^3$ mol$^{-1}$) of individual solution component (either ion or electrolyte) $q$. Since partial molar absorption data of ions and aqueous electrolytes are...
acid chloride and ammonium sulfate, sulfate and potassium chloride, ammonium nitrate in the UV. Krekov black carbon in water. Some species treated here include the following: liquid wavelength-dependent imaginary refractive indices for individual electrolytes and water in solution. Sources of density to the weighted sum of the densities of the individual electrolytes and water in solution. Sources of wavelength-dependent imaginary refractive indices for some species treated here include the following: liquid water [Hale and Query, 1973], organic compounds and black carbon [Krekov, 1993], organic compounds and ammonium nitrate in the UV [Jacobson, 1999c], sodium chloride and ammonium sulfate [Toon et al., 1976], calcium sulfate and potassium chloride [Query, 1987], and sulfuric acid [Palmer and Williams, 1975].

6. 0-D Simulations of the Aerosol/Radiative Algorithms

[32] Here, the processes described above are analyzed in 0-D case studies. In all cases, except for one, the simulations were run with the moving-center size structure. In all cases, the distributions and species considered were those in Tables 1a and 1b. In all cases, five distributions (A, B, D, E1, and F) were initialized. Except where specified, the RH was 90% and the temperature was T = 285 K. Initial distributions are shown in Figure 1. The initial number and mass concentrations, summed over each distribution, were as follows: A, sea spray: 502 cm\(^{-3}\), 54.6 \(\mu g\) m\(^{-3}\) (84% of which was water); B, soil: 6.1 cm\(^{-3}\), 0.72 \(\mu g\) m\(^{-3}\); C, sulfate: 1192 cm\(^{-3}\), 11.2 \(\mu g\) m\(^{-3}\) (82% of which was water); E1, BC < 5% shell: 90 cm\(^{-3}\), 0.25 \(\mu g\) m\(^{-3}\); F, primary organic matter (OM): 337 cm\(^{-3}\), 0.75 \(\mu g\) m\(^{-3}\). These initial conditions represent sea spray particles interacting with low to moderate loadings of soil, sulfate, and OM at a high RH. The initial number and mass concentrations, summed over all distributions, were 2127 cm\(^{-3}\) and 67.5 \(\mu g\) m\(^{-3}\) (82% of which was water), respectively.

6.1. Coagulation Alone

[33] In the first simulation, coagulation alone was simulated for a 12 hour period among the five externally mixed distributions A, B, D, E1, and F to produce larger particles in the same distributions, all possible binary mixtures of distributions (e.g., AB, AD, AE, ...), and higher mixtures (MX). Distributions E2 and E3 were not needed in this simulation, since no growth onto E1 particles was considered. [34] Figure 2a compares the initial and final particle number concentrations, summed over all distributions, resulting from the simulation. The figure appears to indicate, as past coagulation simulations of one size distribution have indicated [e.g., Jacobson, 1997a, Figures 2 and 3], that coagulation among multiple distributions has little effect on the total number concentration of particles larger than 0.2 \(\mu m\) in diameter over a 12 hour period. Figure 2b clarifies this misconception. It shows that coagulation among multiple distributions internally mixes particles of different original compositions, affecting the composition of the entire size distribution without affecting the number concentration of large particles summed over all distributions.

[35] The results shown in Figure 2b suggest that in an air mass containing a moderate loading of particulates, coagulation would produce a larger number concentration of particles larger than 0.2 \(\mu m\).
(a) Number concentration summed over all distributions

(b) Number concentration of each distribution

(c) $S(\text{VI})$ by distribution

(d) $\text{BC}$ by distribution

(e) Soil by distribution
lation alone can internally mix most particles to some degree within 12 hours. In the simulation, coagulation internally mixed almost all the largest particles and a smaller percent of the smaller particles, which may explain a result of Okada and Hitzenberger [2001], who found that the number fraction of mixed particles in Vienna increased with increasing particle radius and with increasing particle abundance.

[36] Not only did coagulation cause a greater fraction of larger particles than smaller particles to mix internally, but it also caused mixtures of larger particles to obtain more components than mixtures of smaller particles. Since the combination of even the smallest with the largest particle is considered a mixture, though, an internally mixed large particle can often contain a trivial amount of a second and/or third component.

[17] Of the total reduction in particle number concentration during the 12 hour simulation, an estimated 97.283% was due to Brownian motion, 2.716% was due to Brownian convective diffusion enhancement, 0.000984% was due to turbulent inertial motion plus turbulent shear, and 0.000089% was due to gravitational collection. Aside from Brownian motion, convective diffusion enhancement had the greatest effect on coagulating small particles with large particles.

[38] Figures 2c–2e show the fate of S(VI), BC, and soil mass concentration by distribution resulting from the simulation. Because S(VI) was initially in two distributions (A and D) whereas BC and soil were initially in one, coagulation spread S(VI) among more distributions than it spread the other components. Figure 2d shows that, although BC did not exist in large particles initially, coagulation of BC with large particles from other distributions put BC into such particles. Most of the largest particles that BC entered contained components from at least two other distributions to form mixed (MX) particles. Figure 2e shows that most large soil particles, which existed initially, coagulated with (most likely) small particles from at least two other distributions to form mixed particles.

6.2. Nucleation and Condensation Alone

[39] Figure 3 shows results when condensation of 1 μg m⁻³ of gas-phase S(VI) (as sulfuric acid) was grown simultaneously onto the five particle size distributions initialized in Figure 1. Homogeneous nucleation of S(VI) was solved simultaneously in distribution D. All nucleated particles were assumed to enter a bin the size of their critical radius and to grow in competition with other particles. Coagulation was ignored in this simulation. The RH was 90% and the temperature was 285 K.

[40] Figures 3a and 3b show that nucleation and growth modified the number and mass concentrations of the sulfate distribution (D) the most. Including nucleation in this case allowed the production of 1.2 × 10⁸ new particles per cubic centimeter during the 12 hour simulation. In the absence of competitive growth, homogeneous nucleation of 1 μg m⁻³ of S(VI) would have produced over 1 × 10⁹ particles cm⁻³ at the critical radius, so solving growth simultaneously with nucleation and conserving mass between the gas and aerosol phases curtailed the runaway particle production that would have been predicted if an explicit calculation were performed. Homogeneous nucleation was not swamped out by growth during the simulation because the initial number concentration of all particles together was not large (2127 particles cm⁻³). Doubling the initial number of particles decreased the number of nucleated particles by more than one half. Thus, as the number concentration of existing particles increased, the more condensation of S(VI) was favored over homogeneous nucleation. Although most new sulfuric acid water particles formed at a diameter near 0.002 μm, condensation onto these particles caused them to grow to around 0.008 μm, as illustrated in Figures 3a and 3b.

[41] Figure 3c shows that growth of S(VI) caused most small BC particles to obtain a shell ≥20% by volume and most midsize BC particles to obtain a shell 5–20% by volume after 12 hours. Only larger BC particles avoided significant growth of S(VI). This result suggests that condensation increases the fractional coating of small particles more than large particles. Condensation similarly affected primarily small OM particles (Figure 3a), soil particles (Figures 3a and 3d), and sea spray particles (Figure 3a).

6.3. Nucleation, Condensation, and Coagulation

[42] Figure 4 shows results when coagulation was added to the simulation of Figure 3, which accounted for homogeneous nucleation and condensation of S(VI). Figure 4a shows that coagulation reduced the distinct nucleation-mode number concentration peak, obtained when coagulation was ignored, by a factor of 40 over the 12 hour period, from 1.2 × 10⁷ particles cm⁻³ in Figure 3 to 3000 particles cm⁻³ in Figure 4. At the same time, coagulation reduced the number concentration of particles >0.3 μm in diameter by only 12%, from 86 to 76 particles cm⁻³.

[43] The large reduction in sulfate particle number concentration when coagulation was included versus when it was not suggests that heterocoagulation during S(VI) nucleation might have caused significant internal mixing of sulfate with other distributions. This can be verified by comparing Figure 4 with Figure 2 (the coagulation-only case). Whereas coagulation alone permitted a large number of BC and soil particles to remain externally mixed (Figures 2c and 2d), coagulation of newly nucleated S(VI) particles internally mixed almost all BC and soil particles (Figures 4c and 4d), producing sulfate–BC particles (DE), soil–sulfate particles (BD), and higher mixtures (MX). This internal mixing was due primarily to coagulation rather than growth because the only source of BD, DE, and MX particles is coagulation. Growth of S(VI) onto primary BC particles (E1) produces E2 and E3 particles. E1, E2, and E3 particles all coagulate with S(VI) (distribution D) to form DE particles. Since the concentrations of E1, E2, and E3 particles were negligible at the end of this simulation, internal mixing of BC must have been due primarily to coagulation, although some of it was due to growth that created E2 and E3 particles, which subsequently coagulated.

6.4. Nucleation, Condensation, and Dissolution/Chemistry

[44] Figure 5 shows results when homogeneous nucleation and condensation of S(VI), dissolution of HCl, HNO₃, and NH₃, internal particle chemical equilibrium and equilibrium hydration were solved between the gas phase and all particle size distributions. The initial concentrations of gas-phase S(VI), HCl, HNO₃, and NH₃ were 1, 0, 0.8, and 0.3 μg m⁻³, respectively. The RH was 90%, and T = 285 K. Simulations with each the moving-center and full-moving
size structures were run. Coagulation was not solved in this case.

[45] Figures 5a.i and 5b show that, in comparison with Figure 3, accounting for additional growth processes caused the newly nucleated S(VI) and other particles to grow to larger sizes than when these processes were ignored. Dissolutional growth and hydration also caused BC particles to obtain larger shell fractions and grow to slightly larger sizes.
Soil similarly grew to larger sizes (Figure 5c versus Figure 3c). Soil similarly grew to larger sizes (Figure 5d versus Figure 3d).

Figure 5e shows the fate of liquid water by distribution. Water uptake was due solely to equilibrium hydration, thus the presence of water in a distribution indicated the distribution contained hygroscopic material by the end of the simulation. Initially, BC, OM, and soil distributions did not contain hygroscopic material. These distributions obtained such material only after S(VI) condensed on them, simultaneously hydrating liquid water. Once liquid water was present, HCl, NH3, and HNO3 could dissolve, changing the solution pH and hydrating more water. Figures 3b and 5b show that S(VI) condensed on the BC, OM, and soil distributions. Figures 5f–5h show that HCl, NH3, and HNO3, respectively, dissolved in the resulting S(VI)–H2O solution. Since no HCl gas existed initially, all the chloride in distributions aside from the sea spray distribution (A) must have evaporated from that distribution to the gas phase then dissolved in the other distributions. Indeed, Figure 5f shows that chloride was lost primarily from small particles in the sea spray distribution (A). This resulted from acidification of the small sea spray particles by sulfate and...

Figure 4. Nucleation, coagulation, and condensation. Same as Figure 3, but when coagulation was treated as well (thus, more distributions were affected).
Figure 5. Nucleation, condensation, and dissolution/equilibrium. (a.i) Number concentrations of seven distributions after 12 hours of nucleation and condensation of S(VI), dissolution of HCl, HNO₃, NH₃, internal particle equilibrium, and equilibrium hydration. The initial gas concentrations of S(VI), HCl, HNO₃, and NH₃ were 1, 0, 0.8, and 0.3 μg m⁻³, respectively, and the RH was 90%. Condensation was solved among all distributions and the gas phase. Nucleation was solved simultaneously with condensation over distribution D. The moving-center size structure was used. (a.ii) Same as (a.i), except the full-moving size structure was used (all nucleated material was placed in the smallest current bin in that case). (b–h) Initial and final mass concentration of (b) S(VI), (c) BC, (d) soil, (e) H₂O(l), (f) Cl⁻, (g) NH₄⁺, and (h) NO₃⁻ in each distribution, all obtained when the moving-center structure was used.
Figure 5. (continued)
nitrates, as shown in Figures 5b and 5h, respectively. The
growth of sulfate and nitrate onto the smallest sea spray
particles simultaneously increased the size of these particles
(Figure 5a.i) so that the smallest sea spray particles not only
grew, but they also lost their chloride.

Figure 5g shows that ammonium entered both small
and large sea spray particles but not particles between
around 0.15 and 1.5 μm. Ammonium entered the small
particles to balance sulfate and other anions in excess of
Na+, Ca2+, Mg2+, and K+. It entered the large particles to
balance the nitrate and other anions in excess of these
cations. Sulfate and nitrate both entered 0.15–1.5 μm
particles, joining chloride there, but these anions were
balanced there by the cations, preventing the dissolution
of ammonia.

Figure 5a.ii shows the final number concentration
distribution for the simulation shown in Figure 5a.i, but
when the full-moving size structure was used. The compar-
ison between the full-moving and moving-center structures
was done because the full-moving structure allows zero
diffusion during growth. However, a problem with the full-
moving structure, illustrated here, is that, once growth
increases the size of the smallest size bin, no real bin exists
for nucleation to occur within. Since the simulation here
included nucleation, all nucleated particles were placed in
the smallest full-moving bin, which was much larger than
the critical radius for nucleation (except at the beginning
of the simulation). In the moving-center structure, a small
bin always exists for nucleation. Thus, the apparent differ-
ence in results in the nucleation mode between the two
simulations is due substantially to the inability to treat
nucleation physically in the full-moving structure. The rest
of the size distribution in both structures are nearly identi-
cal, indicating that the moving-center structure was non-
diffusive yet also treated nucleation physically.

6.5. Nucleation, Condensation, Coagulation, and
Dissolution/Chemistry

Figure 6 shows results when coagulation was added to
the moving-center simulation at 90% RH shown in
Figure 5. Thus, the simulation included nucleation, con-
densation, dissolution, equilibrium chemistry, equilibrium
hydration, and coagulation. A comparison of Figure 6a with
Figure 5a suggests that coagulation reduced the number of
nucleated S(VI) particles, as it did when dissolution
was ignored. This simulation also reaffirms that coagulation
internally mixes a greater fraction of larger particles than
smaller particles and leaves only a residual of externally
mixed small particles unaffected when new sources of those
particles are not considered. After 12 hours, most initial
externally mixed particles from the simulation were intern-
ally mixed with one or more distributions. The sulfate
distribution, which had a new-particle source during the
simulation, remained more externally mixed than did other
distributions, which did not have new-particle sources.
Figure 6b shows that although a good portion of sulfate
remained externally mixed, a large fraction became intern-
ally mixed during the simulation.

Figure 6c shows that only a small amount of BC
remained uncoagulated during the simulation. That BC,
though, was still internally mixed (with greater than 20% coating) due to S(VI) condensation and subsequent hydra-
tion and dissolution. If continuous emissions were treated
simultaneously with the processes described here, distribu-
tion E1 (BC < 5% shell) would always be present to some
degree, as shown by Jacobson [2001]. Figure 6d similarly
shows that only a small amount of soil remained uncoagu-
lated. Figures 6e–6i show the fate of water, soluble species,
and the solid gypsum [CaSO4 · 2H2O(s)]. Gypsum, which
can form when the RH is less than 97%, tied up sulfate in
the sea spray, sea spray–sulfate, and mixed distributions,
reducing the water contents of those distributions.

6.6. Solid Formation During Diurnal Variation of RH

The only solid that could potentially be present at an
initial RH of 95% was gypsum [CaSO4 · 2H2O(s)], which
had a DRH of 97%. Figure 7a shows that it formed initially
in the sea spray distribution and was present to some degree
at all RHs. Figures 7a and 7b show that the water content
decreased with decreasing RH and increased with increas-
ing RH, as expected. Water content was higher for a longer
period during a decrease in RH than for an increase in RH,
particularly in the sea spray distribution, since a metastable
state was assumed during a decrease in RH but not an
increase. Assuming a metastable reduced solid formation in
comparison with not assuming one, increasing liquid water
content. The most abundant solids formed in the sea spray
distribution were NaCl(s), gypsum, and NaNO3(s). In the
sulfate distribution, which did not contain Na+, Mg2+, Ca2+,
or K+ because coagulation was ignored), the primary solids
were NH4HSO4(s) and (NH4)2SO4(s). Much more NH4+
entered the sulfate distribution than the sea spray distribu-
tion because the sea spray distribution had more cations
there initially. More NO3− entered the sea spray distribution
than the sulfate distribution for the opposite reason. Al-
though no HCl existed in the gas phase and no Cl−
existed in the sulfate distribution initially, some Cl−
was transferred from the sea spray distribution to the gas phase
then to the sulfate distribution, as shown in Figure 7b.

6.7. Refractive Indices and Solution Densities

Figures 8a and 8b show solution and total particle
real refractive indices, weight percent solute in solution,
solution pH, and solution density for the sea spray distrib-
ution (A) after a simulation in which condensation of
S(VI), dissolution of HCl, HNO3, NH3, internal particle
Figure 6. Nucleation, coagulation, condensation, and dissolution/equilibrium. Same as Figure 5, but when coagulation was treated as well. The moving-center structure was used to obtain these results.
Figure 6. (continued)
equilibrium, and equilibrium hydration were treated at 90% and 40% RH, respectively. Coagulation was ignored. Figures 8c and 8d show the concentrations of species in the sea spray distribution in the two cases, respectively, at the time of the refractive index calculations. The difference between the solution and total particle refractive indices for the sea spray distribution is the refractive indices due to solids, since they are not in solution.

Figure 8a shows that the difference between solution and total refractive indices at 90% RH was small. This was because the solution volume dominated the total particle volume at 90% RH. The only nonsolution component of the particles in that case was gypsum. The weight percent solute in the distribution peaked at about 0.1 µm diameter. Because water has a lower density and refractive index than do most electrolytes dissolved in solution, solution density and refractive index also peaked at about 0.1 µm.

Figure 8b shows that the increase in weight percent solute with decreasing particle size was greater at 40% RH than at 90% RH, causing the solution density to increase with decreasing particle size more at 40% RH than at 90% RH. At all particle sizes, solids comprised a greater percent of particles at 40% RH than at 90% RH. At 40% RH, the solid fraction increased with decreasing particle size. Due to the high solid fraction at 40% RH, the total particle real refractive index at all particle sizes was about 7% higher than was the solution real refractive index, and both were higher than the total or solution refractive indices at 90%.
RH. Solid electrolytes enhanced the real refractive index compared with when the electrolytes dissolve in solution because when electrolytes dissolved, they hydrated water, and the real refractive index of water is less than that of most solid electrolytes.

Although real refractive indices of particles with solutions decrease with increasing RH, scattering extinction coefficients of such particles increase with increasing RHs [e.g., Tang et al., 1997], because particle cross sections increase with increasing RHs.

7. Conclusions

This paper discussed numerical techniques for solving coagulation, simultaneous nucleation and condensation, and nonequilibrium dissolution/equilibrium reversible chemistry...
over multiple size distributions. All schemes conserve moles (including between the gas and aerosol phases) or volume, are unconditionally stable, and except for the reversible chemistry scheme, noniterative. The schemes, previously used in a global 3-D climate study [Jacobson, 2001], were applied here in a zero-dimensional box model to analyze the effect of (1) coagulation alone, (2) nucleation plus condensation alone, (3) nucleation, condensation, and coagulation, (4) nucleation, condensation, dissolution/reversible chemistry, and (5) nucleation, condensation, coagulation, dissolution/reversible chemistry, all among multiple aerosol size distributions and the gas phase. Some results of the study were:

1. Coagulation internally mixes particles of different original composition over the entire size distribution.
2. Coagulation internally mixes a greater fraction of larger particles than smaller particles.
3. Coagulation internally mixes larger particles with a greater number of other distributions than it does smaller particles.
4. Coagulation among multiple distributions produces the same summed size distribution as coagulation of a single distribution when the sum of the initial distributions are the same in both cases.
5. In a competition for available vapor between homogeneous nucleation and condensation, the relative importance of condensation increases with an increasing number of background particles.
6. In the absence of a continuous source of new particles, coagulation, condensation, dissolution, hydration, and chemical reaction internally mix most particles within half a day under moderately polluted conditions.
7. Condensation increases the fractional coating of small particles more than it does large particles.
8. The real refractive index of a particle containing electrolytes is higher at low RHs than at high RHs.
9. The difference between the real refractive index of a total particle containing electrolytes and its solution component increases with decreasing RH.
10. The real refractive index of a solution generally increases with decreasing particle size.

[58] Acknowledgments. This work was supported by the NASA New Investigator Program in Earth Sciences, the Environmental Protection Agency, the National Science Foundation, the David and Lucile Packard Foundation and the Hewlett-Packard Company, and the Stanford University Office of Technology and Licensing.

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