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GCEP-GREF End of Summer Workshop
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Aerosols and Climate Change

Radiative Forcing Components

- Long-lived greenhouse gases
  - CO₂: 1.06 [1.49 to 1.63], Global, High
  - N₂O: 0.48 [0.43 to 0.53], Global, High
  - CH₄: 0.10 [0.14 to 0.16], Global, High
  - Halocarbons: 0.54 [0.31 to 0.97], Global, High

- Ozone
  - Stratospheric: -0.05 [-0.15 to 0.05], Continental to global, Med
  - Tropospheric: 0.35 [0.25 to 0.65], Continental to global, Med

- Stratospheric water vapour from CH₄: 0.07 [0.02 to 0.12], Global, Low

- Surface albedo
  - Land use: -0.2 [-0.4 to 0.0], Local to continental, Med
  - Black carbon on snow: 0.1 [0.0 to 0.2], Local to continental, Med

- Total Aerosol
  - Direct effect: -0.5 [-0.9 to -0.1], Continental to global, Med
  - Cloud albedo effect: -0.7 [-1.8 to -0.3], Continental to global, Med
  - Linear contrails: 0.01 [0.003 to 0.03], Continental, Low

- Solar irradiance: 0.12 [0.09 to 0.16], Global, Low

- Total net anthropogenic: 1.6 [0.8 to 2.4], Global, Low

IPCC Climate Change 2007: The Physical Science Basis, Summary for Policy Makers, pg. 16.
Aerosols and Climate Change
Aerosol Size Classifications

- Fine Particles
- Ultra-fine Particles
- Nucleation Mode
- Aitkin Mode
- Accumulation Mode
- Coarse Particles

Formed by gas phase condensation
Aerosol Size Classifications

- **Fine Particles**
  - Nucleation Mode
  - Aitkin Mode
  - Accumulation Mode

- **Ultra-fine Particles**

- **Coarse Particles**
  - 0.01 μm
  - 0.1 μm
  - 2.5 μm
  - 10 μm

Growth of ultra-fine particles by monomer condensation or coagulation of clusters
Aerosol Size Classifications

- **Fine Particles**
- **Ultra-fine Particles**
- **Coarse Particles**

Nucleation Mode: 0.01 μm
Aitkin Mode: 0.1 μm
Accumulation Mode: 2.5 μm

- Direct and cloud albedo effect
- Tropospheric lifetimes of 1-2 weeks
Nucleation

- Onset of a phase transition
- Atmospheric nucleation by gas to particle conversion
- Homogeneous nucleation: condensation of vapors or atoms to form small liquid droplets
- Heterogeneous nucleation: coagulation of atoms or molecules onto existing aerosol.
Nucleation Events

Ion Induced Nucleation: ~0.5% of particle current at 1nm.
<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>Condensation Nuclei/Particle Counters</td>
<td>CNC or CPC</td>
<td>optical particle sizing</td>
<td>activation of particles by vapor condensation - growth to detectable sizes</td>
<td>3 nm</td>
</tr>
<tr>
<td>Differential Mobility Analyzer</td>
<td>DMA</td>
<td>electrical mobility size selection</td>
<td>ions seperated by electrical mobility</td>
<td></td>
</tr>
<tr>
<td>Scanning Mobility Particle Sizer</td>
<td>SMPS</td>
<td>electrical mobility size selection, optical detection</td>
<td>aerosol charger, DMA and CPC combination</td>
<td>detection of charged species limited by detector (CPC, electrometer)</td>
</tr>
<tr>
<td>Aerosol Mass Spectrometer</td>
<td>AMS</td>
<td>optical or aerodynamic particle sizing, mass-to-charge species characterization</td>
<td>aerodynamic lenses, optical and/or time of flight sizing, thermal or laser desorption for mass filtration</td>
<td>18 nm</td>
</tr>
<tr>
<td>Aerosol Time of Flight Mass Spectrometer</td>
<td>ATOFMS</td>
<td>aerodynamic particle sizing, mass-to-charge species characterization</td>
<td>aerodynamic diameter infered from optical detection, mass filtration</td>
<td>50 nm (down to 30 nm at low detection efficiencies)</td>
</tr>
<tr>
<td>Thermal Desorption Chemical Ionization Mass Spectrometer</td>
<td>TD-CIMS</td>
<td>mass-to-charge species characterization</td>
<td>desorbed particles are broken into constituent ions for mass filtration</td>
<td>4 nm</td>
</tr>
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Atmospheric Nucleation

- Nucleated clusters are roughly 1 nm in diameter
- Growth to 3 nm occurs on the order of minutes up to an hour

- Uncertainties due to measurement gap:
  - Physical conditions at time of nucleation
  - Species responsible for nucleation
  - Species responsible for growth to detectable sizes
Measurement Objective

Value at Monomer Size Anchored by Measured [H$_2$SO$_4$]

Collision-Controlled Theory

Cluster CIMS

new Nano-SMPS

Measured Size Distribution
Atlanta, 8/19/02, 11:00
(existing Nano SMPS)

\( \frac{dN}{d\log D_p}, \text{cm}^{-3} \)

\( D_p, \text{nm} \)
Sulfuric Acid Correlation

- $\text{SO}_2 + \text{OH}$ (from $\text{O}_3$ photolysis) $\rightarrow \text{H}_2\text{SO}_4$
- Clustering of Hydrated $\text{H}_2\text{SO}_4$ occurs under atmospherically relevant conditions
- Observations show similar diurnal patterns for “detectable” particles and $\text{H}_2\text{SO}_4$
Sulfuric Acid Correlation

\[ \frac{dN}{d\log D_p}, \text{ cm}^{-3} \]

\( D_p, \text{ nm} \)

\( [\text{H}_2\text{SO}_4], 10^6 \text{ cm}^{-3} \)

\( [\text{OH}], 10^6 \text{ cm}^{-3} \)

\( N_{[3,11]} \)

\( N_{\text{tot}} \)
Beyond Binary

- Particle production rates are often orders of magnitude higher than rates predicted by the binary nucleation of sulfuric acid and water.
- Recent nucleation theories have focused on the ternary nucleation of H₂SO₄-H₂O-NH₃ system
- Laboratory studies show enhanced nucleation of sulfuric acid-water in presence of ppb concentrations of NH₃
- Freshly nucleated particles are composed mainly of ammonium sulfate in certain atmospheric regions
- New particle growth rates may be a factor of 2 to 10 times higher than can be explained by the condensation of sulfuric acid and associated water and/or ammonia molecules onto particles.
Reaction Chamber
• 1000 L
• Teflon film reactor
• Temperature controlled casing
• Photochemical production of H₂SO₄
• Atmospherically relevant precursor gas concentrations
• Sufficient reaction time to reach steady state

Cluster-CIMS Schematic

CIMS Inlet
• “Soft” chemical ionization, intact cluster
• Transverse ion drift field – neutral cluster detection
• Nitrogen sheath flow to minimize water condensation

Mass Filter
• Octopole focusing assembly – transport of intact clusters, gas compression
• Quadrupole mass filter
• Channel electron multiplier
**Cluster-CIMS Schematic**

**Reaction Chamber**
- 1000 L
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**CIMS Inlet**
- “Soft” chemical ionization, intact cluster
- Transverse ion drift field – neutral cluster detection
- Nitrogen sheath flow to minimize water condensation
Cluster- CIMS Measurements

Objectives

- Steady state $\text{H}_2\text{SO}_4$–$\text{H}_2\text{O}$ cluster distributions
- Temperature, humidity, precursor concentration dependence
- Effect of NH$_3$, organic amines on cluster distributions
- Atmospheric measurements of freshly nucleated clusters (NCAR- Boulder, CO)
Theoretical Approach
Population Balance Equations

\[
\frac{dN_1}{dt} = R - N_1 \sum_{j=1}^{\infty} \beta_{1j} N_j + \sum_{j=2}^{\infty} (1 + \delta_{2j}) E_j N_j - \gamma A_{Fuchs} N
\]

\[
\frac{dN_k}{dt} = \frac{1}{2} \sum_{i+j=\text{odd}}^{\infty} \beta_{ij} N_i N_j - N_k \sum_{i=1}^{\infty} \beta_{ik} N_i + E_{k+1} N_{k+1} - E_k N_k - \frac{\gamma A_{Fuchs}}{\sqrt{k}} N_k
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The condensation rate ($\beta$) is multiplied by an accommodation coefficient ($\alpha$), here it is assumed that $\alpha=1$.
Population Balance Equations

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**Assumptions:**

• Dependent on a single species
• All collisions are effective
• Evaporation derived from bulk liquid properties
Summary

- “Bridge the Gap” - molecular clusters to particles
- Field Studies – first quantitative measurements of neutral molecular clusters in continental troposphere
- Laboratory Studies – binary, ternary systems and beyond
- Theoretical Component- analysis of accommodation and evaporation coefficients, empirical input to current modeling of new particle formation
Acknowledgements

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Chongi Kwang, Univ. MN
Particle Technology Laboratory, Univ. MN

NSF-NRIT, Grant No. ATM-0506674
• Steady state cluster distribution: solve population balance equations, separate accommodation and evaporation

• Evaporation depends on the internal energy of the cluster vs. the surroundings: cluster composition and temperature.

• Accommodation depends on monomer production rate through the frequency of molecular collisions.

• Hold temperature constant, vary monomer production rate: observe changes in distribution and attribute those to accommodation, using Chongai Kuang’s models.

• Once size dependent accommodation coefficients are known: vary temp to look at size dependent evaporation rates.