Using Measurements of CCN Activity to Characterize Mixing State, Chemical Composition, and Droplet Growth Kinetics of Atmospheric Aerosols

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Motivation: What’s Important for CCN?

How well do we understand the aerosol-CCN link?

What is the level of aerosol complexity required to “get things right”? (Size, Chemical Composition, etc.)

How much “inherent” indirect effect uncertainty is associated with different treatments of complexity?

Method of approach:

- Use in-situ data to study the aerosol-CCN link.

- Quantify the uncertainty in predicted CCN associated with assumptions taken in models.

- See if we are missing anything.
When Would Aerosols Form Droplets?

Solute Concentration (M)

Relative Humidity (%)

Wet aerosol diameter (µm)

Credit: A. Nenes
When Would Aerosols Form Droplets?
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$\text{CCN} = f (\text{Size, Chemical Composition})$

Equilibrium line for a 20 nm ammonium sulfate particle

Critical %SS

Critical Wet Diameter

Wet Aerosol (Haze)

Cloud Droplet

Relative Humidity (%) vs. Wet aerosol diameter (µm)
How many particles will act as CCN in a cloud?

Sc vs Dp graph: composition and size impacts of Köhler theory

Typically, CCN(s) looks like a “sigmoid” - it’s actually $(1 - \text{erf}(s))$ for lognormal single-mode aerosol, which looks “sigmoidal”.
How do we measure CCN?
Streamwise Thermal-Gradient CCN Chamber

- Metal cylinder with wetted walls
- Streamwise Temperature Gradient
- Water diffuses faster than heat
- Supersaturation, $S$, generated at the centerline = $f$ (Flowrate, Pressure, and Temp. Gradient)

$S = \frac{P_{H_2O}(T_1)}{P_{sat H_2O}(T_0)}$

Roberts and Nenes (2005)
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Outlet: [Droplets] = [CCN]

Roberts and Nenes (2005)
Conventional Method of Operation

- Typically, $dT/dz$ is varied, with Flowrate, Pressure = constant
- Significant lag time: Data discarded
- Limited number of $\%SS$s
- Poor time (and spatial) resolution!

ARCPAC Data: April 15, 2008

%SS = 0.32  %SS = 0.21  %SS = 0.10

240 km @ 200m s$^{-1}$ (NOAA P3)
The Streamwise Thermal-Gradient Cloud Condensation Nuclei Counter

- Metal cylinder with wetted walls
- Streamwise Temperature Gradient
- Water diffuses faster than heat

Supersaturation, $S$, generated at the centerline = $f$ (Flowrate, Pressure, and Temp. Gradient)

... so why not change the flow rate instead of temperature gradient (A LOT faster)?

Roberts and Nenes (2005)
Done! We call it: Scanning Flow CCN Analysis (SFCA)

Operation:
- Flowrate is linearly ramped over user-specified upscan, peak, and downscan time intervals
- Temp. gradient, Press. = const.
- Can be combined with a DMA to select a single particle size and/or a CPC to measure CN

Analysis/Results:
- CCN response curves similar to those obtained by stepping supersaturation
- Complete CCN spectrum in less than 30 seconds! (versus ~ hr.)
Some issues we were concerned with:

Limitations set by physics:
- Let simulations figure out if:
- Scanning too fast kills growth
- Counting statistics
- If transients dominate the growth (challenging the inversion).

Limitations set by the hardware of the instrument:
- Detection limitations in activated droplets
- Integration time in the OPC.

Simulations suggest the best compromise between speed and resolution.
Model Simulations of SFCA

Scan time limited by characteristic diffusion timescale,

\[ \tau \propto \frac{r^2}{D} \approx 10 \text{ seconds} \]

“Pseudo-steady state” behavior is expected down to 10 s ramps.

This ensures robust activation of CCN and their detection.
Experimental Data: Monodisperse AS Aerosol

60-Second Ramps

- 50 nm ammonium sulfate particles selected by DMA
- Upscan: $t_{\text{scan}} \sim 28s$
- Downscan: $t_{\text{scan}} \sim 136s$
  (Green Curve)
- Excellent agreement between simulated and measured activated ratios!
- Outlet droplet sizes plateau and then decrease with decreasing residence time (flowrate), increase with increasing residence time

Experimental Data: Monodisperse AS Aerosol

Very Sharp Activation Curves.

Supersaturation in instrument depends linearly on (instantaneous) flow rate.

The method is robust and agrees very well with expectations.

60-Second Upscan Ramps
Works equally well with 10s scans.

Experimental Data: Roof of Ford ES&T Building

Excellent qualitative agreement between Scanning Flow CCN Analysis (SFCA) and Conventional Stepping-Temperature-Mode.

Complete CCN spectrum obtained in 10 to 60 seconds versus 75 minutes!

Experimental Data: Roof of Ford ES&T Building

60-second Scan 10-second Scan versus 1¼ hour per spectrum using the conventional technique

Value of Size-Resolved CCN Measurements

CCN Spectra provide a lot of information:

- Chemical Heterogeneity (Mixing State)
- Average Organic Properties (e.g., Molar Mass, Solubility)
- Droplet Growth Kinetics
- Surface Tension Depression

To obtain this information, need to compare CCN Activation and Droplet Growth at as a function of size and at multiple supersaturations!
Different “Modes” of Expressing CCN Data

Fix size, vary s

Or fix s, and vary size

Continuous monitoring at the Georgia Tech Rooftop Measurement Platform in Midtown Atlanta from December 2008 – June 2009

- Condensation Particle Counter (CPC)
- DMT CCN Chamber (CCNC) using Scanning Flow CCN Analysis

Ground based study (AMIGAS) in Atlanta, GA from August – Sept. 2008

- Particle-into-Liquid Sampler (PILS)
- Condensation Particle Counter (CPC)
- DMT CCN Chamber (CCNC) using Scanning Mobility CCN Analysis
Size-Resolved CCN Number Concentration Timeseries from Midtown Atlanta, March 8-14, 2009

- Concentrations measured from approximately 0.2 - 1% supersaturation
- 5 different DMA sizes, each for three minutes
- Size distribution centered around 80nm – 100 nm.
Diurnal Hygroscopicity and Mixing State Trends in Midtown Atlanta, March 8-14, 2009

- **S**: Slope, C: degree of chemical heterogeneity of the activated particles
- **1-E**: Inflection point, S*: “characteristic” cutoff supersaturation
- **Maximum, E**: Fraction of hygroscopic externally mixed particles

**Graphs:**
- Graph 1: Activated Ratio (CCN/NC) vs. Instrument Superaturation
- Graph 2: Maximum Activated Ratio (E) vs. Eastern Standard Time
- Graph 3: Chemical Variability Exponential Constant (C) vs. Eastern Standard Time
- Graph 4: Critical Supersaturation (S*) vs. Eastern Standard Time
CCN Closure: Comparing Observations with Predictions from Theory

Measured composition from PILS/TOC & Assumptions: Mixing State, Surface Tension, Organic Properties

+ Measured size distribution from SMPS

= Predicted CCN Concentration

Does the predicted concentration match what we measure?
CCN Closure Scenarios

Four CCN closure scenarios considered correspond to typical assumptions in regional models:

1) Composition Type Assumptions:
   - **All ammonium sulfate** – aerosol is composed of solely (NH₄)₂SO₄.
   - **Only salts soluble** – only the inorganic salts present in the aerosol are soluble.
   - **All soluble** – all compounds in the aerosol are soluble.
   - **All soluble + surface tension** – all compounds in the aerosol are soluble and the organics are allowed to suppress surface tension by 25%.

2) Composition Size-Dependence Assumptions:
   - **Size averaged** – all particles have the same composition regardless of size.
   - **Size resolved** – each particle size has a particular composition.

3) Mixing State Assumptions:
   - **Internal mixture** – chemical compounds are distributed uniformly across the entire particle population; all particles have the same composition.
   - **External mixture** – chemical compounds exist in some particles but not others; individual particles fall into compositional types.
Best closure: when only salts is assumed soluble. We know though that organics depress surface tension and contribute solute.
Overestimation on CCN concentration highly influenced by the assumption that all sizes have the same hygroscopic fraction (external mixture). However this is not the case.

Therefore, can introducing size-resolved mixing state data improve predictions?
Introducing Mixing State Into The Closure

External Mixture of Two Aerosol Types:

Soluble Fraction ($E$): Composition from PILS

Insoluble Fraction ($1 - E$): No soluble mass
Introducing size resolved mixing state improves the CCN closure significantly.
Summary

Scanning-Flow CCN Analysis: A new way to obtain FAST CCN spectra

– Insensitive to the uptake coefficient
– Requires only one flow tube.
– Scan time can be as fast as counting statistics and droplet detection allow (~10s).

We see a strong diurnal variation in maximum CCN concentration (E) and also cutoff supersaturation, suggesting the presence of a less-hygroscopic, externally-mixed aerosol during the morning.

Noticeable decrease in cutoff supersaturation in the afternoon which suggests that particles become more hygroscopic as the day progresses.

The best agreement between observed and predicted CCN concentrations is achieved using size-resolved mixing state assumptions and assuming all species are soluble.

Our study agrees with other urban city results (e.g., Houston, Mexico City, Riverside, and Tokyo) which have found aerosols to be externally mixed:

  Neglecting mixing state in such environments could lead to CCN (and therefore cloud droplet) overestimation.
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Fast Size-Resolved CCN Measurements (SMCA)