Quantifying the impact of surfactants on cloud condensation nuclei activity with a particle-resolved model

Xiaotian Xu, Jeffrey H. Curtis, Nicole Riemer
Department of Atmospheric Science, University of Illinois Urbana-Champaign

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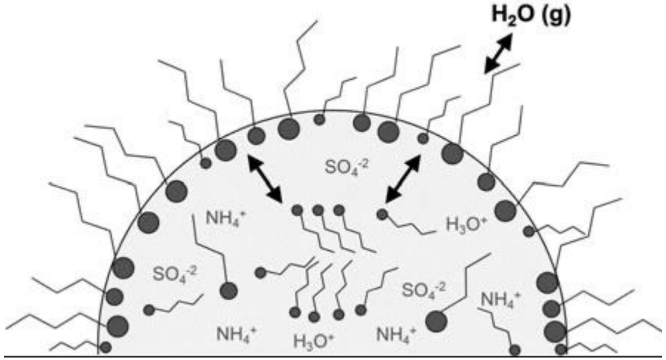
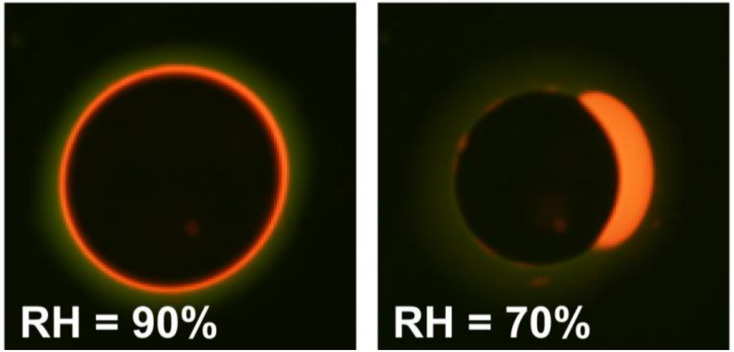
What are surfactants?

“Surfactants are chemicals that reduce surface tension of medium where it dissolved and/or interfacial tension with different phases”

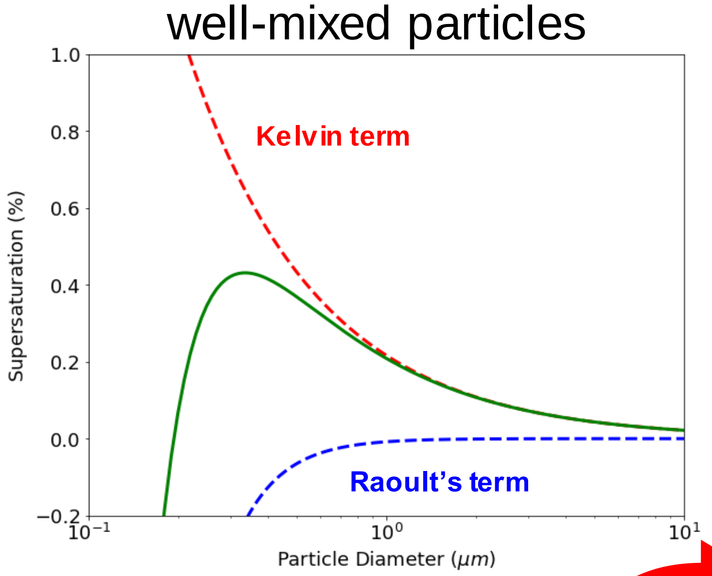




- ➢ Surfactants are partitioned to surface.
- ➢ Full cover as organic films; partially engulfed inorganic core.
- ➢ Surfactants can impact CCN activity of aerosols.

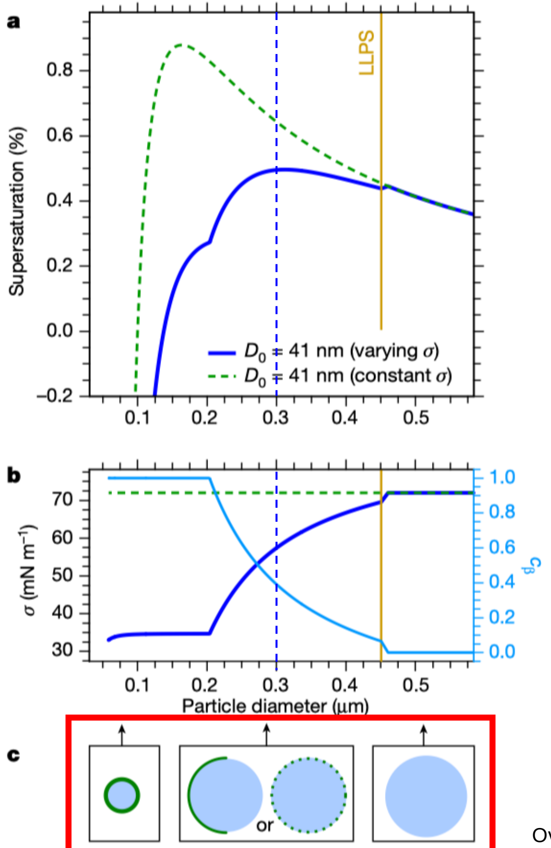
McNeill et al., Top Curr Chem, 2013
Freedman, Chem Soc Rev, 2017

Activation process for different particle mixing rules



$$S(D) = \frac{D^3 - d^3}{D^3 - (1-\kappa)d^3} \exp\left(\frac{4\sigma_{s/a} M_w}{RT\rho_w D}\right)$$

$$\sigma_{s/a} = \sigma_w$$



particle with film

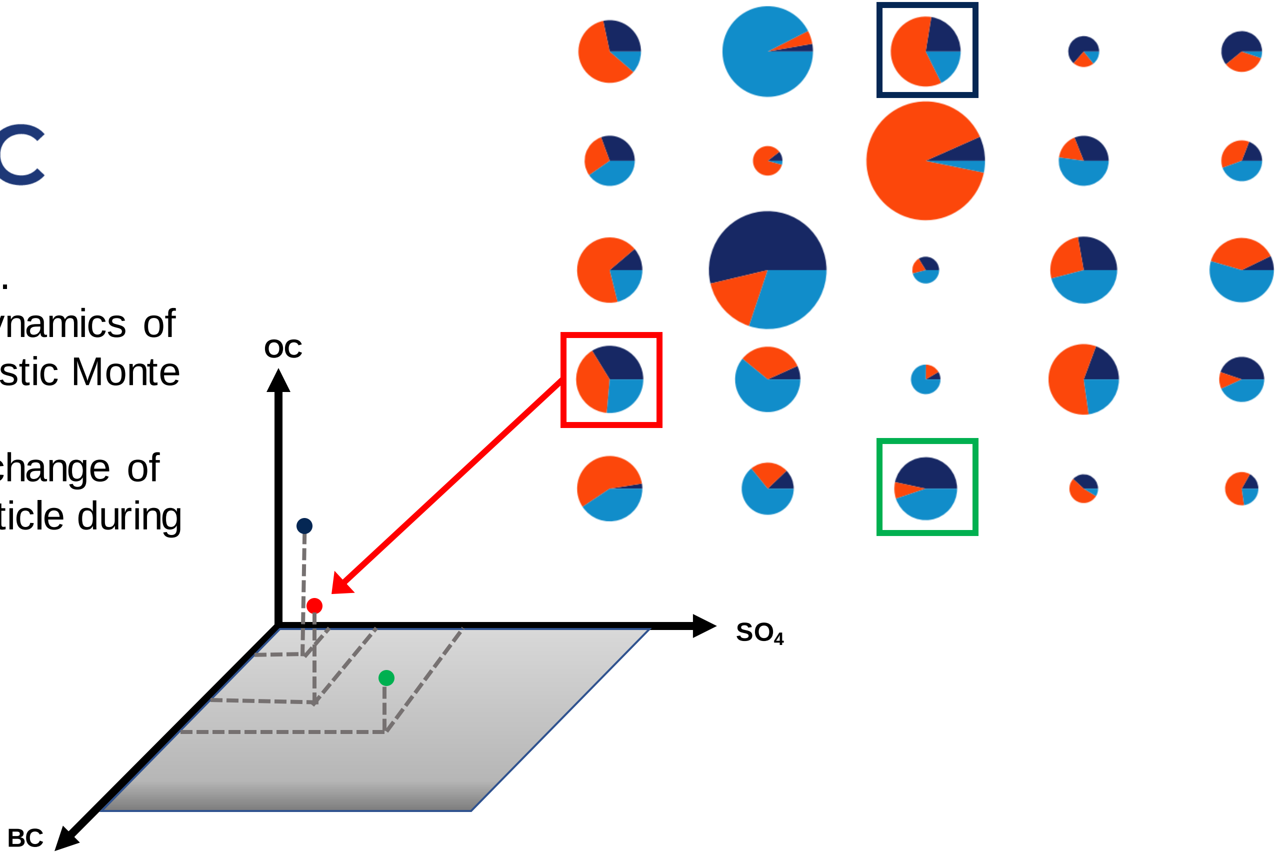
Pettersand Kreidenweis, 2007

Ovadnevaite et al, Nature, 2017

Particle-resolved aerosol model PartMC-MOSAIC

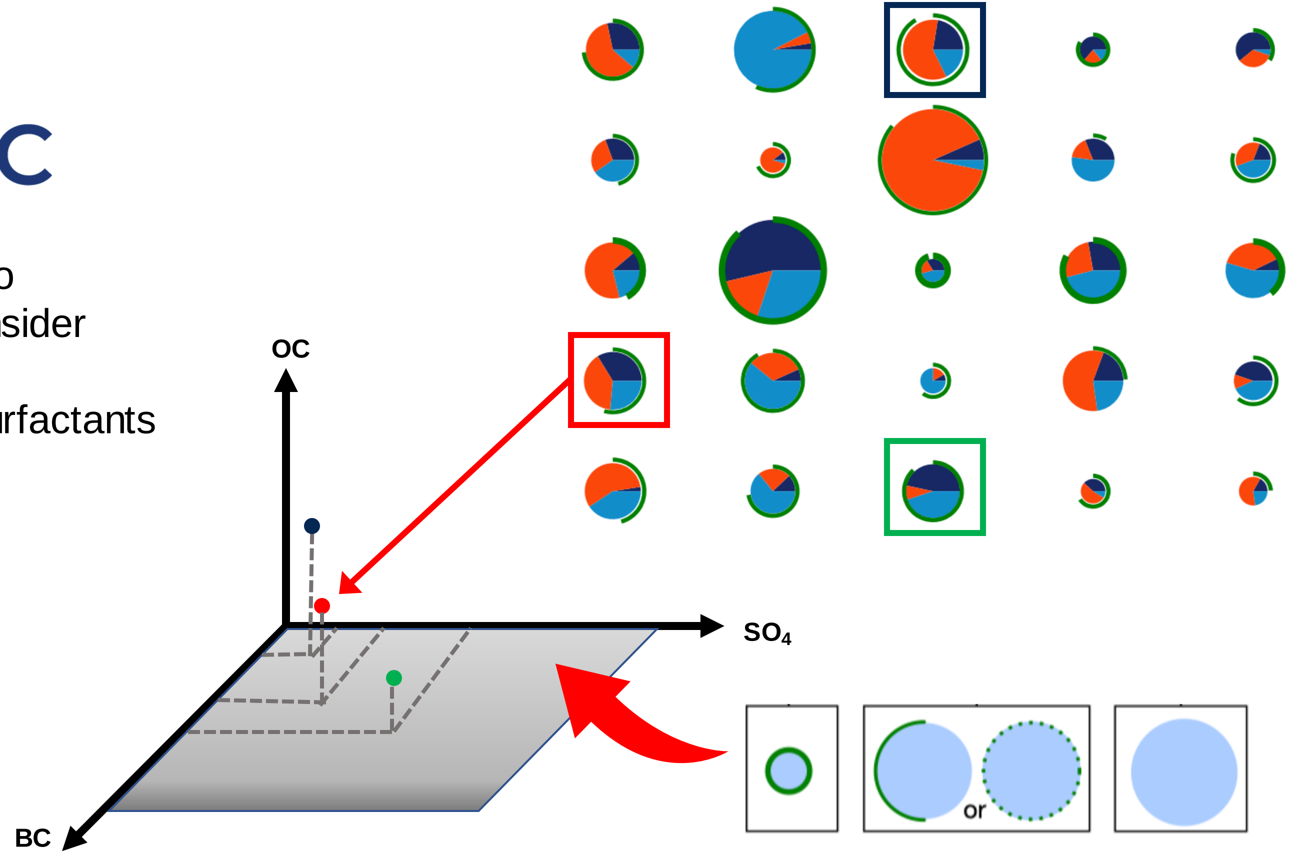
PartMC

- A Lagrangian box model.
- PartMC simulates the dynamics of an aerosol with a stochastic Monte Carlo approach.
- MOSAIC simulates the change of composition of each particle during the evolution.



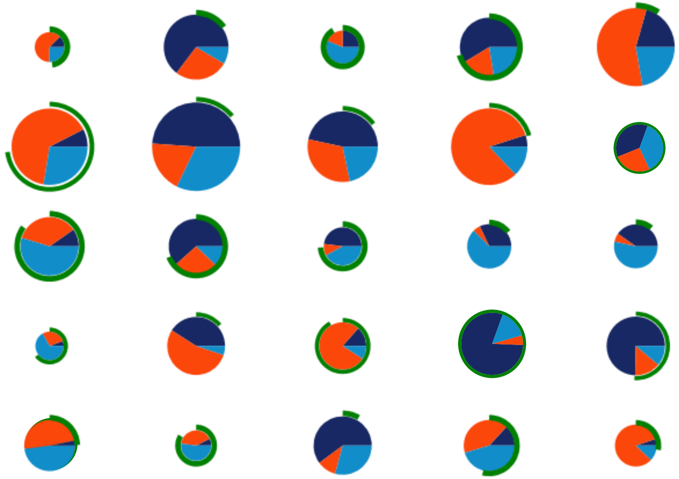
Our goal of this research

- Implement a method into PartMC-MOSAIC to consider surfactants
- Quantifying impact of surfactants on CCN activity



How to represent surface tension for each particle?

Surfactants impact surface tension of each particles, thus not constant surface tension (CST) anymore.

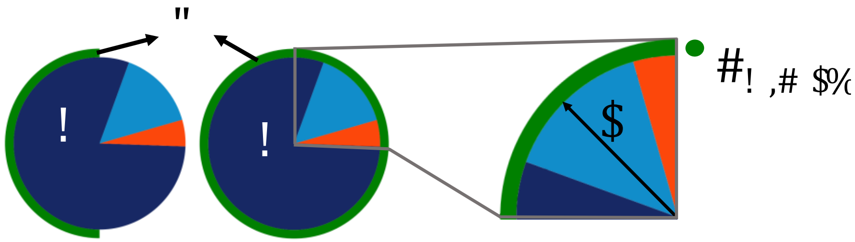


$\boldsymbol{\sigma \neq \sigma_w}$ →

$$S(D) = \frac{D^3 - d^3}{D^3 - (1-\kappa)d^3} \exp\left(\frac{4\sigma M_w}{RT\rho_w D}\right)$$

$\boldsymbol{\sigma}$ **?**

Effective surface tension (EST) method



$$\sigma(D) = (1 - C_\beta)\sigma_\alpha + C_\beta \sigma_\beta$$

Effective surface tension

a) Morphology Assumption

Liquid-Liquid Phase Separation (LLPS)

Core: inorganic-rich phase α

Shell: organic-rich phase β

b) Minimum Shell Thickness

phase β must be at least of a certain thickness

$\delta_{\beta,\,min} \in [0.16, 0.3]$ nm

c) Surface Coverage

$$C_\beta = \min\left[\frac{V_\beta}{V_\delta}, 1\right]$$

Shell volume: $V_\delta = \frac{4}{3}\pi\left[(r + \delta_{\beta,\,min})^3 - r^3\right]$

Ovadnevaite et al, Nature, 2017

Finding root for new critical supersaturation

$$S(D) = \frac{D^3 - d^3}{D^3 - (1-\kappa)d^3} \exp\left(\frac{4\sigma_w M_w}{RT\rho_w D}\right)$$

$$\frac{\partial S(D)}{\partial D} = \frac{-Af(D)}{D^2(D^3-(1-\kappa)d^3)^2} \exp\left(\frac{A}{D}\right) = 0$$

$$f(D) = D^6 - \frac{3d^3\kappa}{A}D^4 - (2-\kappa)d^3D^3 + (1-\kappa)d^6 = 0$$

$$A = \frac{4\sigma_w M_w}{RT\rho_w}$$

$$\frac{\partial f(D)}{\partial D} = 6D^5 - \frac{12d^3\kappa}{A}D^3 - 3(2-\kappa)d^3D^2$$

Newton's iteration

critical diameter D_c

critical supersaturation S_c

$$S(D) = \frac{D^3 - d^3}{D^3 - (1-\kappa)d^3} \exp\left(\frac{4\sigma(D)M_w}{RT\rho_w D}\right)$$

$$\frac{\partial S(D)}{\partial D} = \frac{-\tilde{A}\tilde{f}(D)}{(D^3-(1-\kappa)d^3)^2 D^2} \exp\left(\frac{\tilde{A}\sigma(D)}{D}\right)$$

$$\tilde{f}(D) = R(D)(D^6 - (2-\kappa)d^3D^3 + (1-\kappa)d^6) - \frac{3d^3\kappa}{\tilde{A}}D^4$$

$$R(D) = \sigma(D) - D\frac{\partial\sigma(D)}{\partial D}$$

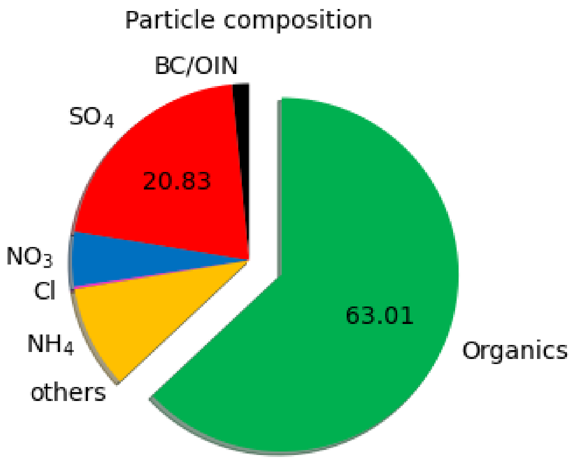
$$\tilde{A} = \frac{4M_w}{RT\rho_w}$$

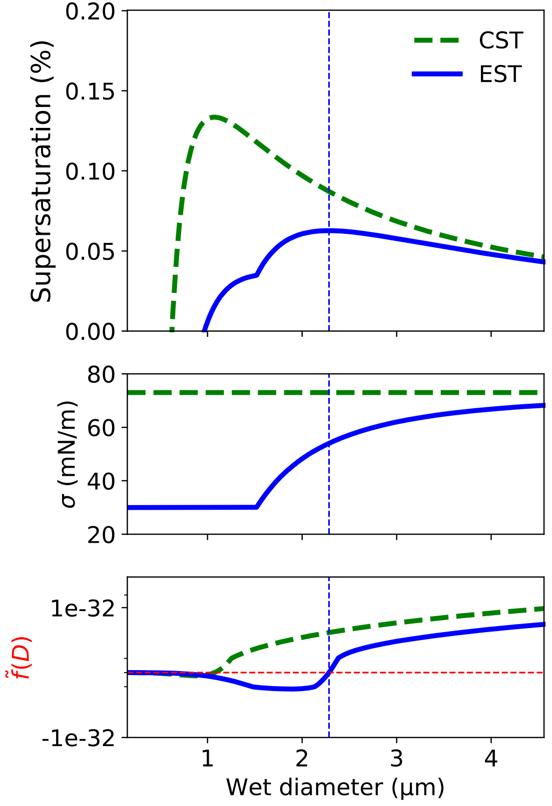
$$\frac{\partial \tilde{f}(D)}{\partial D} = \frac{\partial R(D)}{\partial D}(D^6 - (2-\kappa)d^3D^3 + (1-\kappa)d^6) + R(D)(6D^5 - 3(2-\kappa)d^3D^2) - \frac{12d^3\kappa}{\tilde{A}}D^3$$

critical diameter D_c, S_c

Comparison of Köhler curve with/out EST

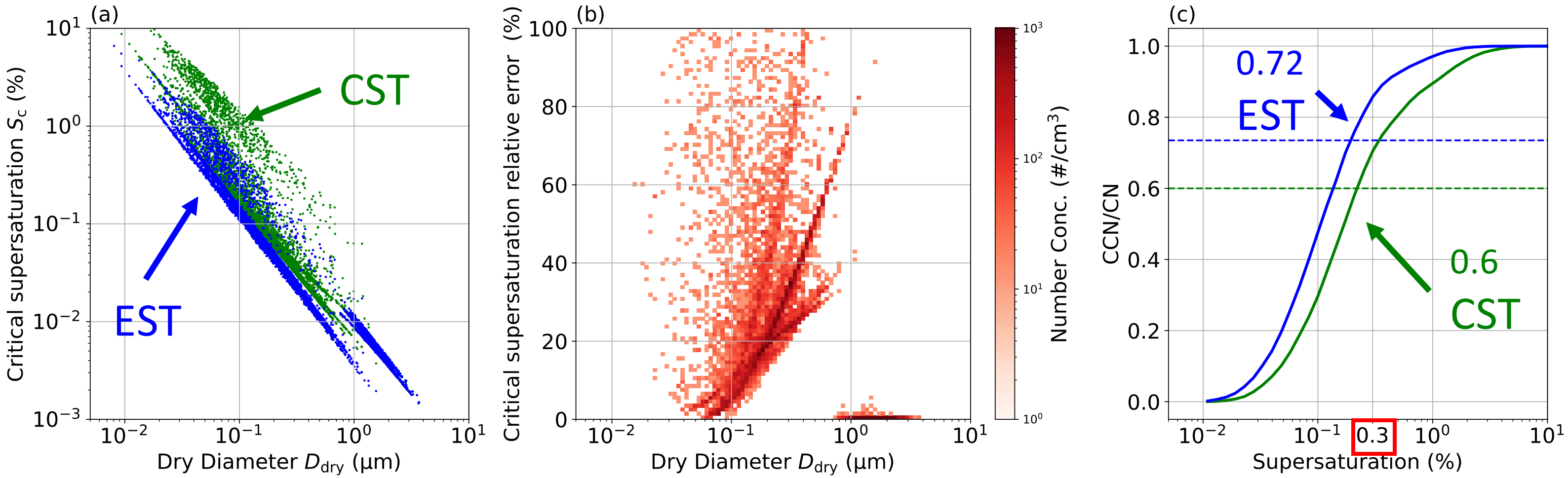
Example case





- A 0.15 μm dry particle with composition shown in pie chart.
- critical supersaturation in this case lowered by ~45%.
- σ at critical supersaturation is ~54 mN/m.

A 24h idealized urban plume scenario simulation considering a population of 10000 computational particles. Time = 12h here.

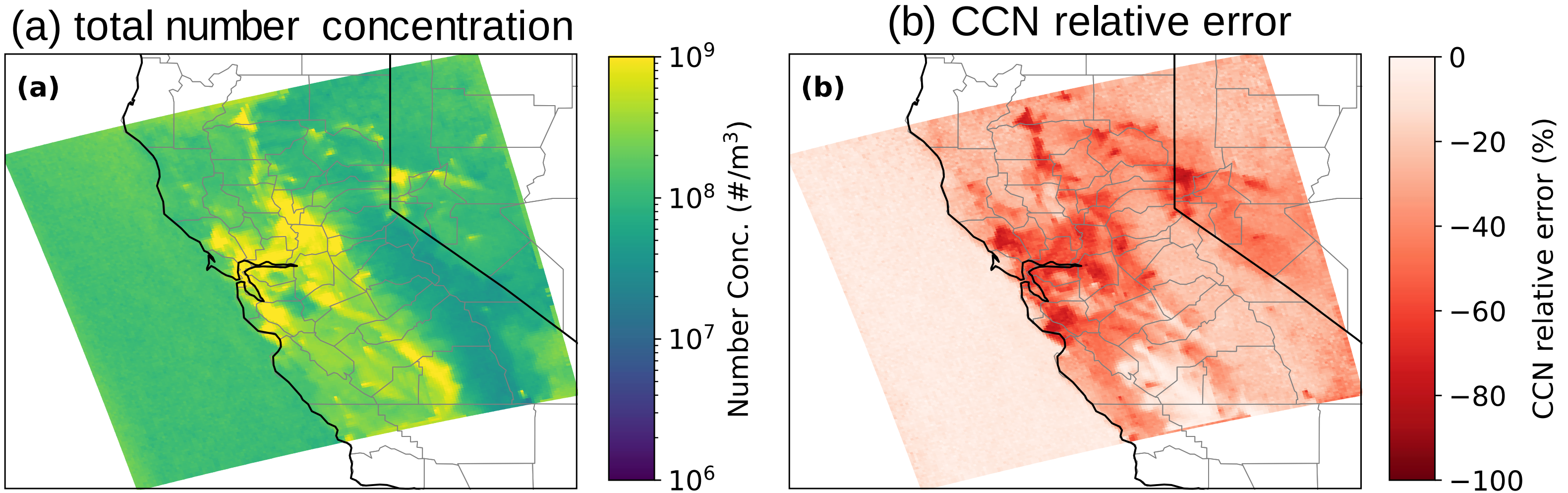


- ➢ Comparison of S_c as a function of D_{dry} with CST and EST for t = 12h.
- ➢ Relative error in critical supersaturation with an average of 57%.
- ➢ Activation ratio at 0.3% is 0.73 for EST, while 0.6 for CST.

Impacts on regional scale - near surface

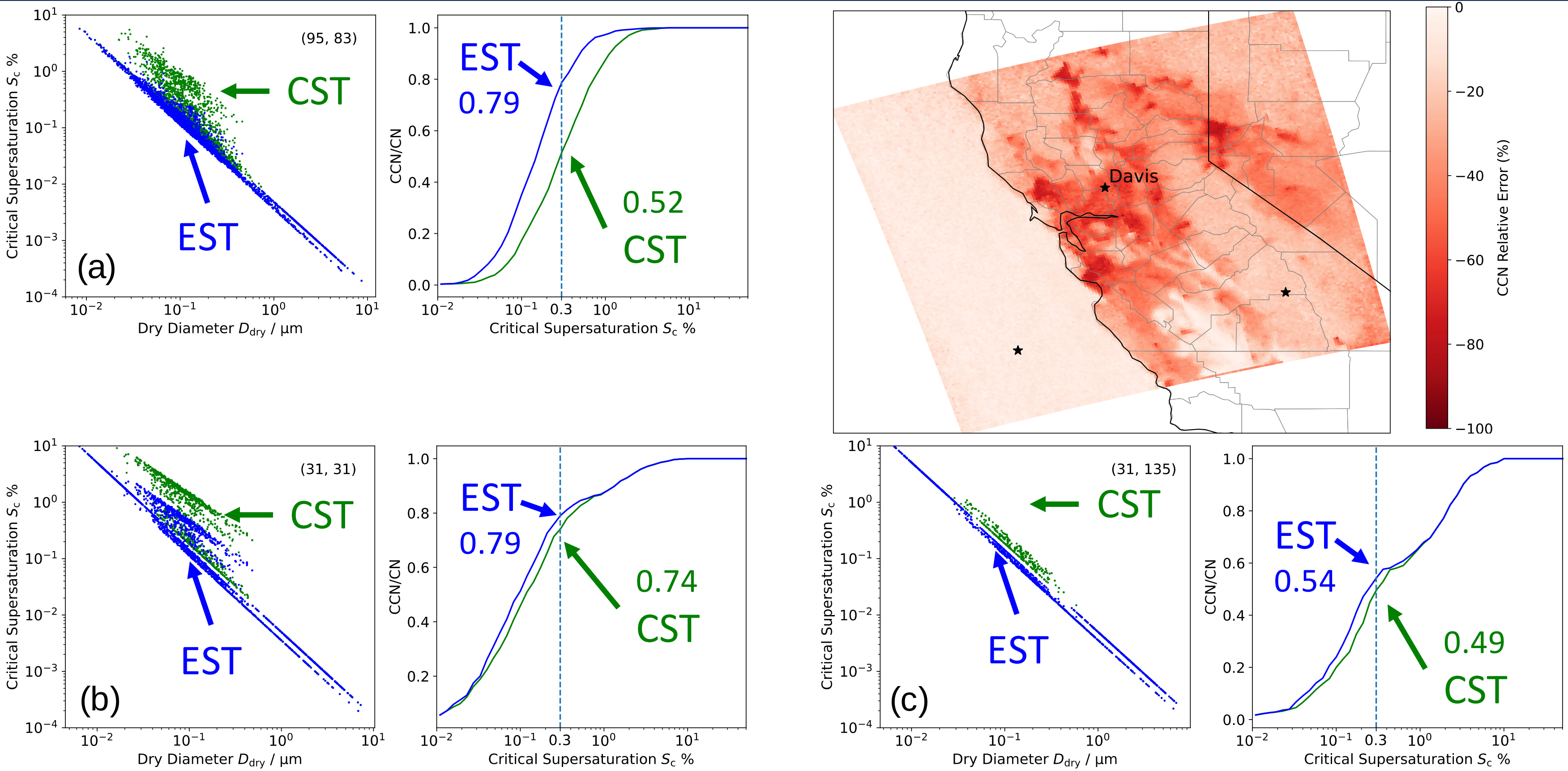
Apply EST method to WRF-PartMC simulation results.

$$\varepsilon_{\mathrm{CCN}} = \frac{CCN_{\mathrm{EST}} - CCN_{\mathrm{CST}}}{CCN_{\mathrm{EST}}}$$

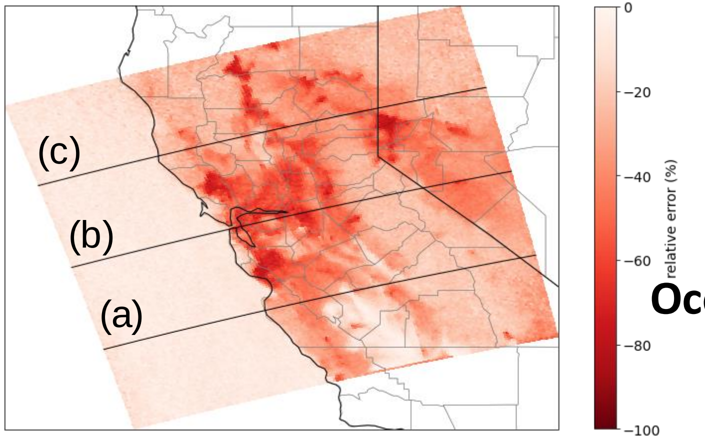


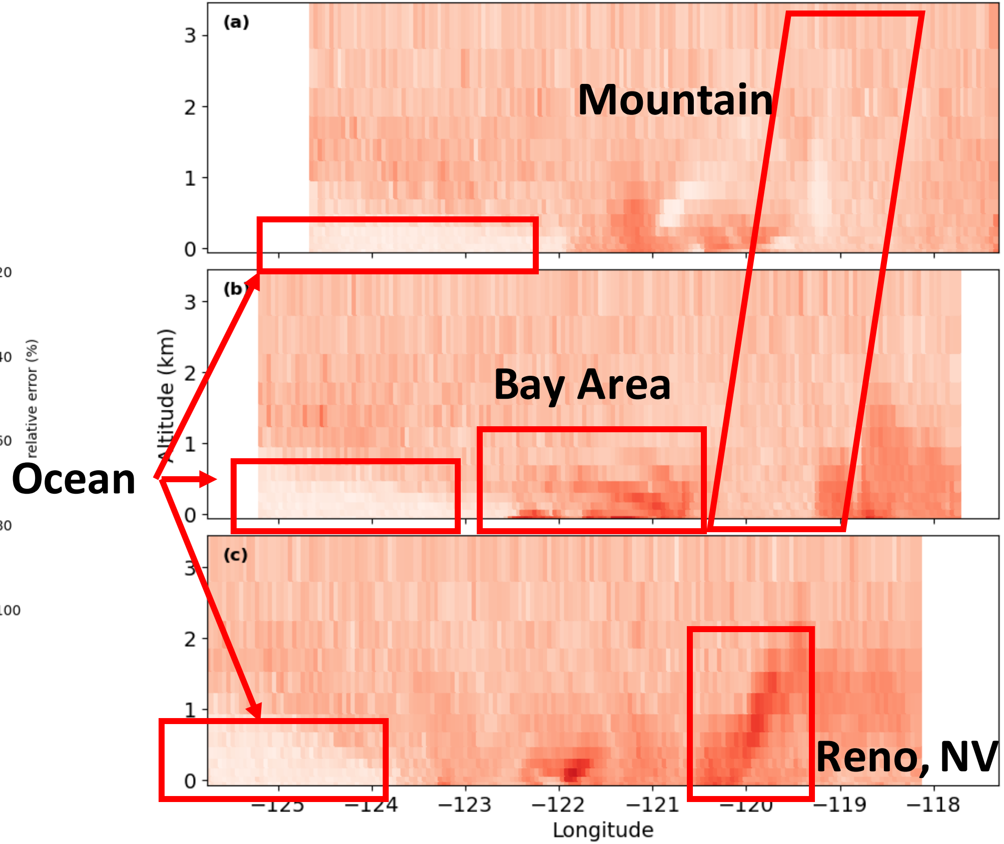
- The average relative error is ~24%.
- The highest relative error is ~85%.

Impacts on regional scale – different locations



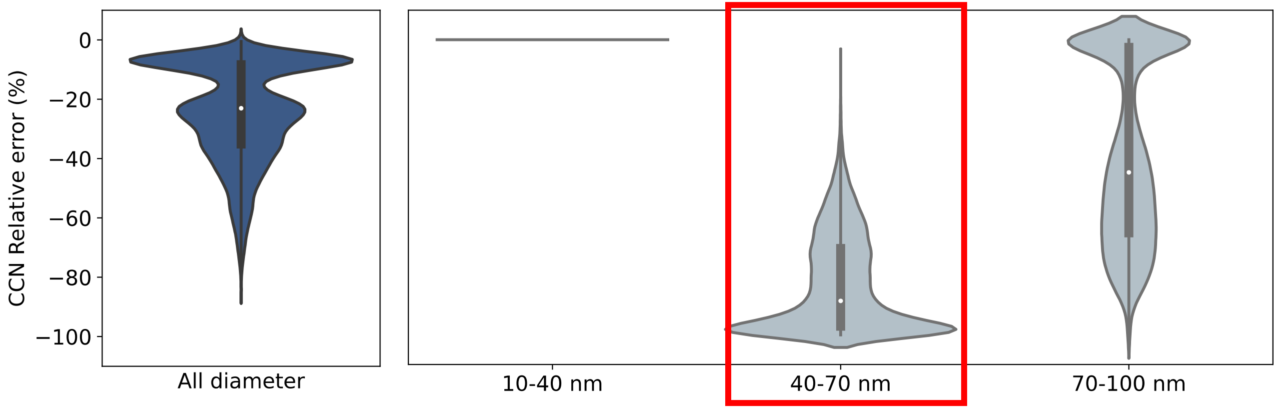
Impacts on regional scale - vertical level





Impacts on regional scale – PDF

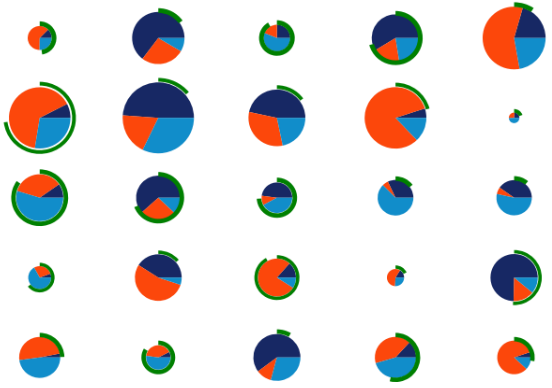
Apply PDF to CCN concentration relative error for whole simulation region



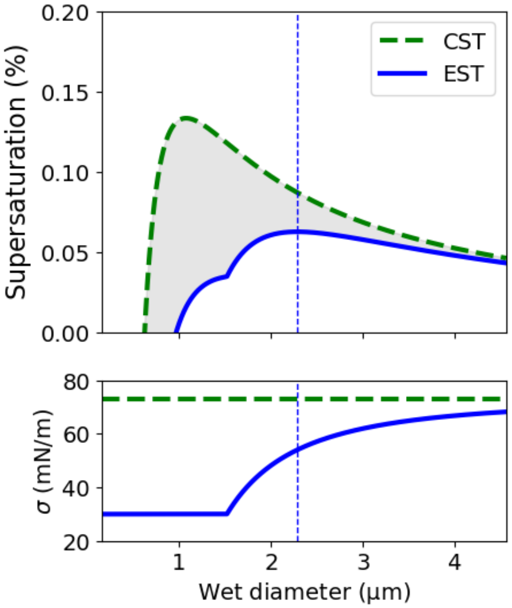
- PDF for all diameter: largest frequency occurs at ~10%.
- The greatest relative error in CCN concentration occurs within the 40 − 70 nm size interval.

Conclusions

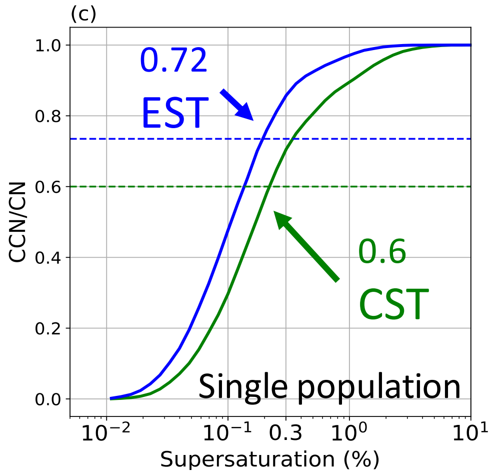
PartMC



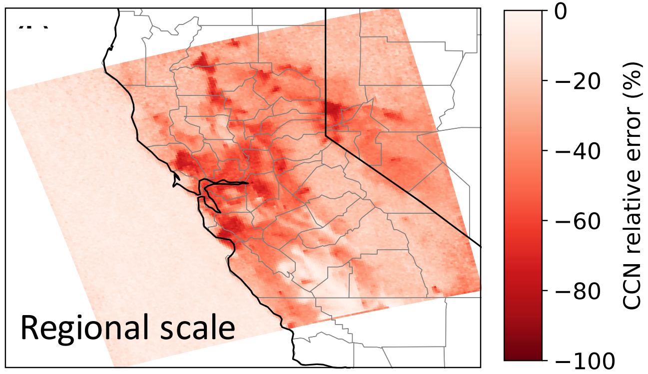
Model development



Single particle scale



Single population



Regional scale

Future work

- Previous κ-Köhler theory provides upper limit.
- Current effective surface tension method provides lower limit.
- Apply O:C ratio to replace LLPS assumption.
- Refine SOA scheme to capture species with high O:C ratio.

Thank you! Questions?

Xiaotian Xu
xx24@illinois.edu
xiaotianxu.com