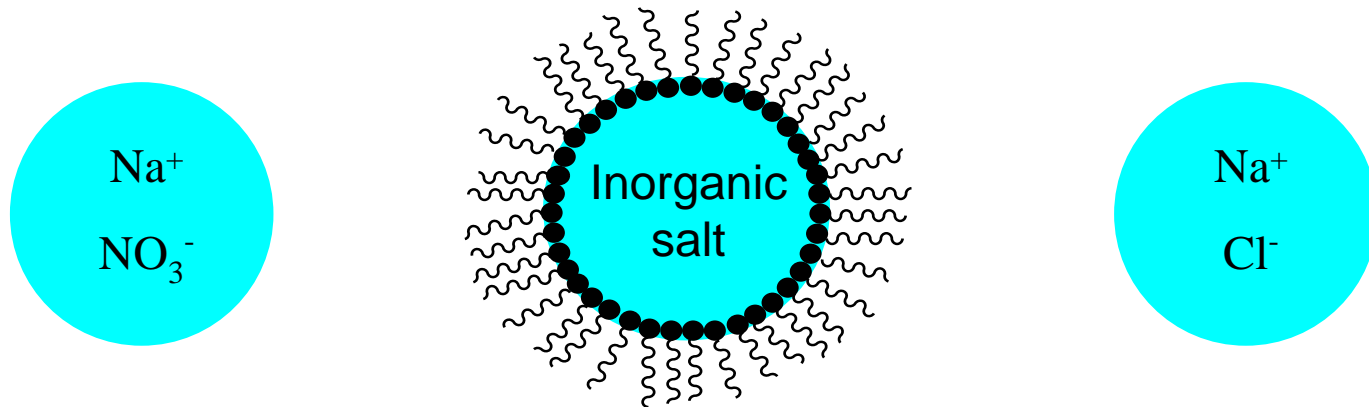


Effects of Soluble Surfactants on Density, Shape and Water Uptake of Common Hygroscopic Particles



Luis A. Cuadra-Rodríguez
University of Colorado at Boulder
CGEP End-of-Summer
August 14th, 2007

Gracias

- GCEP-GREF (Milton, Jeff, Staff)
- B. Ellison and Ellison's group
- Alla Zelenyuk (PNNL-EMSL)
- DOE-Basic Science

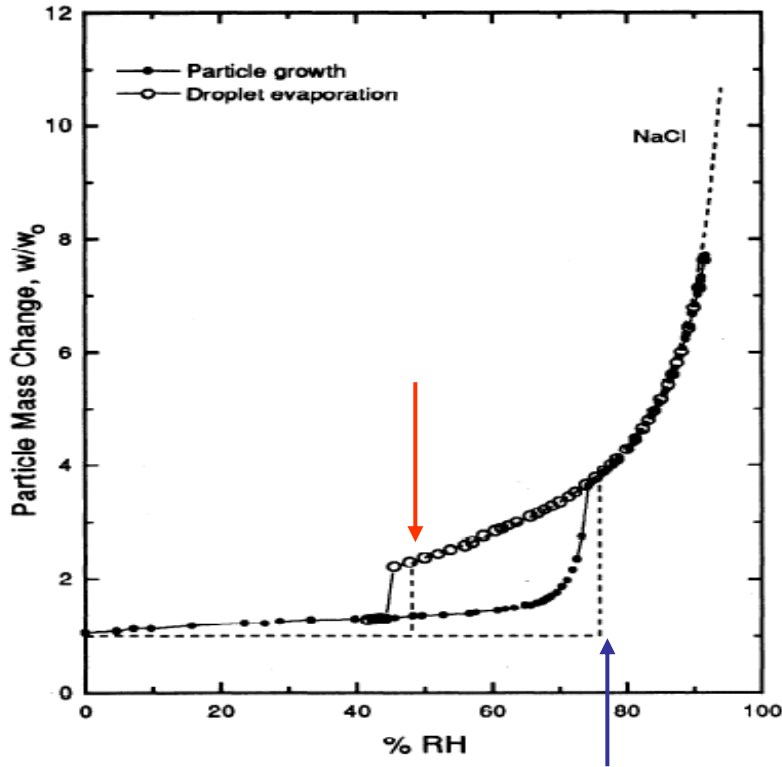


Inorganic Particles' Properties

- **Physical** and Chemical properties
- Efflorescence → relative humidity at which particles lose all the water and crystallized. (liquid→solid)
- Deliquescence → relative humidity at which particles gain water and become a droplet. (solid→liquid)
- Growth Factors (GFs)

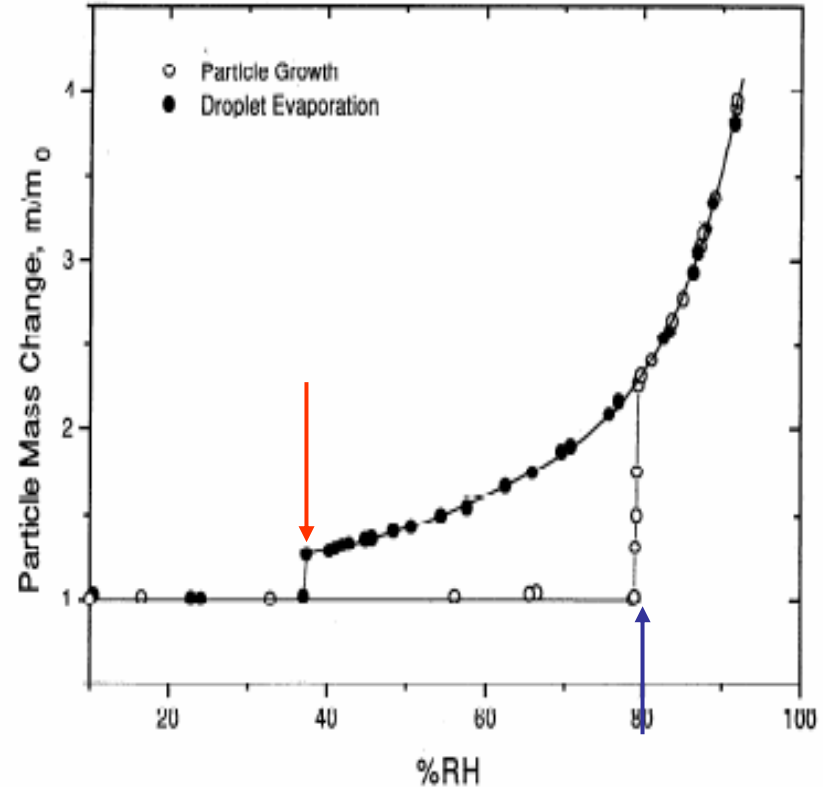
Sub-micron-size Particles Properties

Sodium Chloride, Na^+Cl^-



Efflorescence ~ 42% RH
Deliquescence ~ 78% RH

Ammonium Chloride, $(\text{NH}_4^+)_2\text{SO}_4^{2-}$

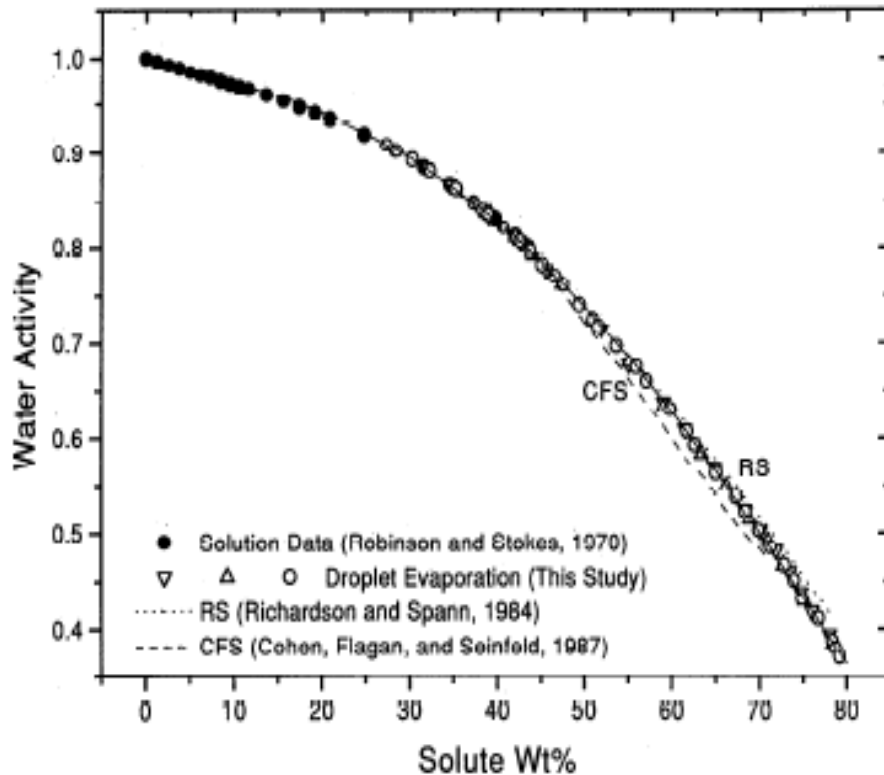
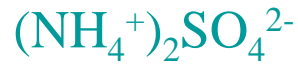


Efflorescence ~ 37-40% RH
Deliquescence ~ 80% RH

Tang, I.N.; Munkelwitz, H.R. *J Geophys. Res-Atmos* 1994, 99(D9): 18801-18808

Tang, I.N.; Tridico, A.C.; Fung, K.H. *J Geophys. Res-Atmos* 1994, 102(D19): 23269-23275

Micron-sized Particles Properties



$$a_w = 1.00 + \sum C_i w f_i$$

$$RH = 100 a_w$$

$$\rho = 1.00 + \sum A_i w f_i$$

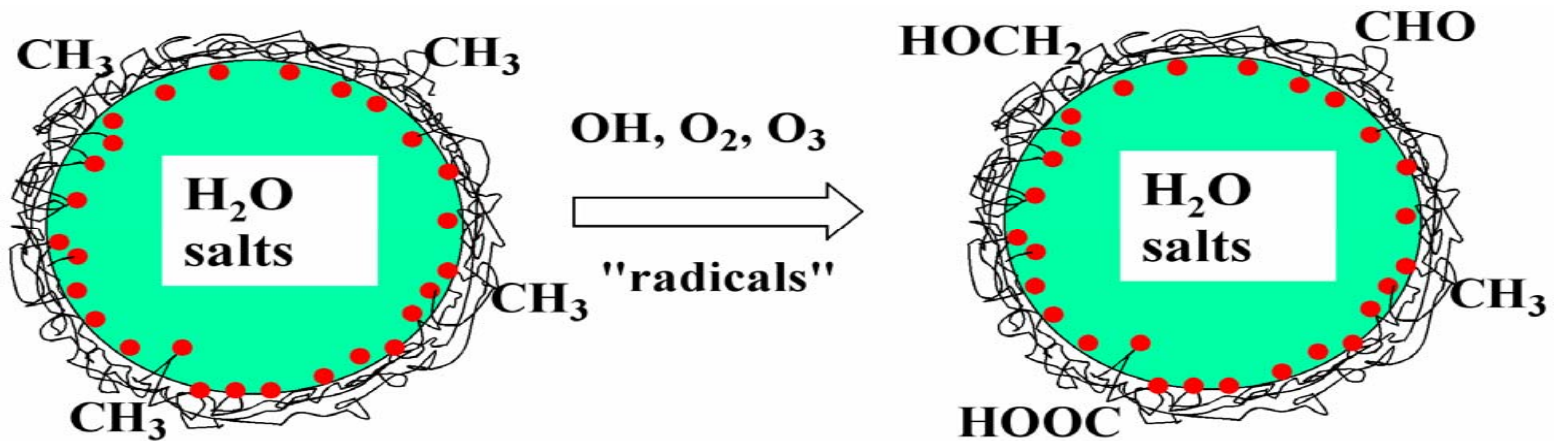
$$d_{ve}^3 = \left(\frac{(w f) \rho_p}{\rho_{salt}} \right) d_m^3$$

$$d_{ve} = \sqrt[3]{\left(\frac{(w f) \rho_p}{\rho_{salt}} \right)} d_m$$

$$\frac{d_{ve}}{d_m} = \sqrt[3]{\left(\frac{(w f) \rho_p}{\rho_{salt}} \right)}$$

Tang, I.N.; Munkelwitz, H.R. *J Geophys. Res-Atmos* 1994, 99(D9): 18801-18808

Tang, I.N.; Tridico, A.C.; Fung, K.H. *J Geophys. Res-Atmos* 1994, 102(D19): 23269-23275

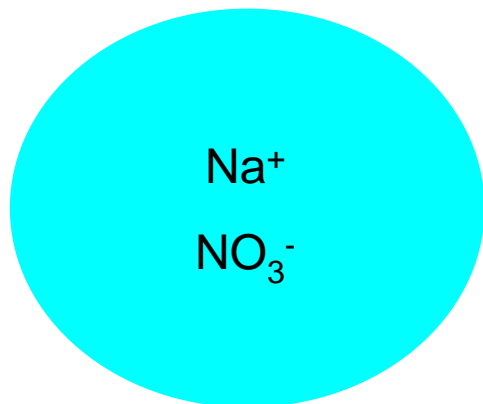


- A large fraction of atmospheric particles are composed of common hygroscopic inorganic salts (sulfates, nitrates, sea salts) that are mixed with a variety of organics.
- *Surfactants* – coat particle's surface, alter particles' interactions with the atmosphere (gas species, water vapor), CCN activity, change size and optical properties as a function of RH.
- It is important to quantitatively characterize these particles' behavior as a function of RH

Surfactant effects-Previous work

- *Growth Factors (GFs)* – HTDMA work showed that the addition of organics to inorganics does NOT prevent water uptake or loss but the amount gained or loss. (Hansson *et al.* (1999), Chen & Grace (1999 & 2001))
 - Larger organic fraction → lower GFs
 - Deliquescence points are lower compare to pure salt.
- CCN activity – surfactants did “alter” $(\text{NH}_4)_2\text{SO}_4$ particle activation, did NOT inhibit it, except for stearic acid.

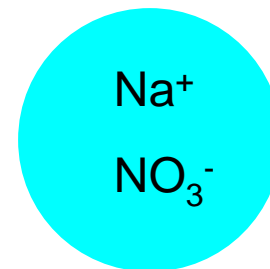
Approach



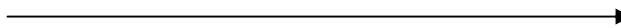
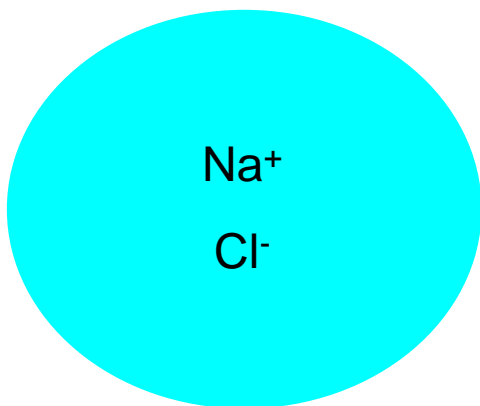
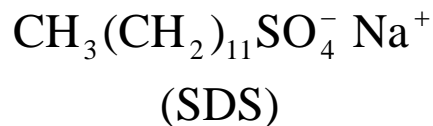
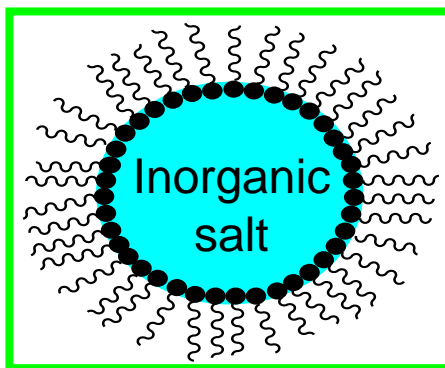
Drop



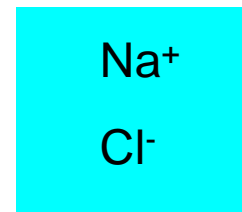
No shape factor



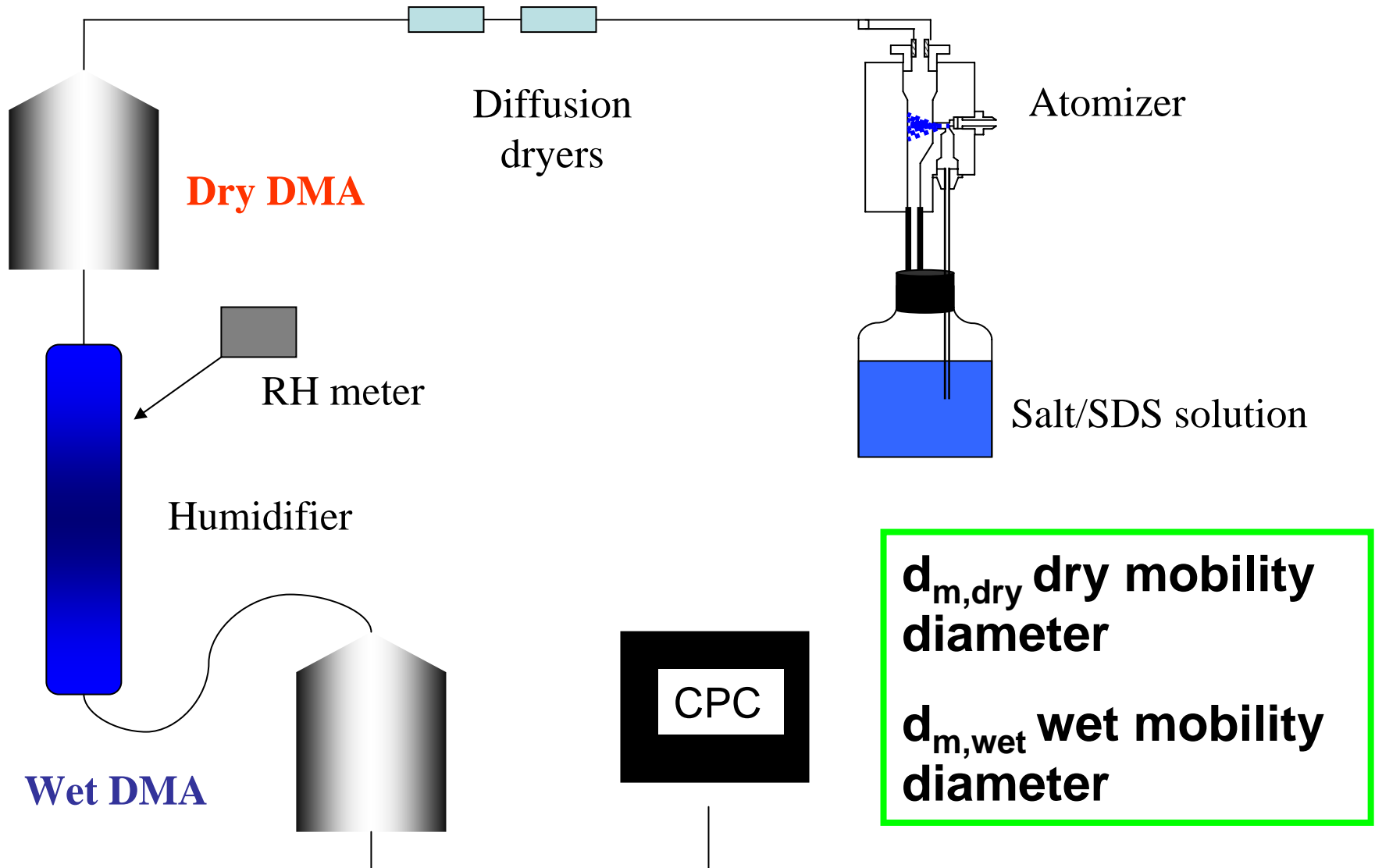
Dry particle



Shape factor



Experimental (GFs)



Density

$$\rho_p = \rho_0 \frac{d_{va}}{d_m}$$

$$\rho_{eff} \equiv \frac{d_{va}}{d_m} = \frac{\rho_p}{\rho_0} \frac{1}{\chi^{-2}} \frac{C_c(d_{va} \bar{\chi} \rho_0 / \rho_p)}{C_c(d_m)}$$

$$\frac{1}{\chi^{-2}} = 1.094 \frac{\rho_{eff}}{\rho_p} - 0.096$$

GFs

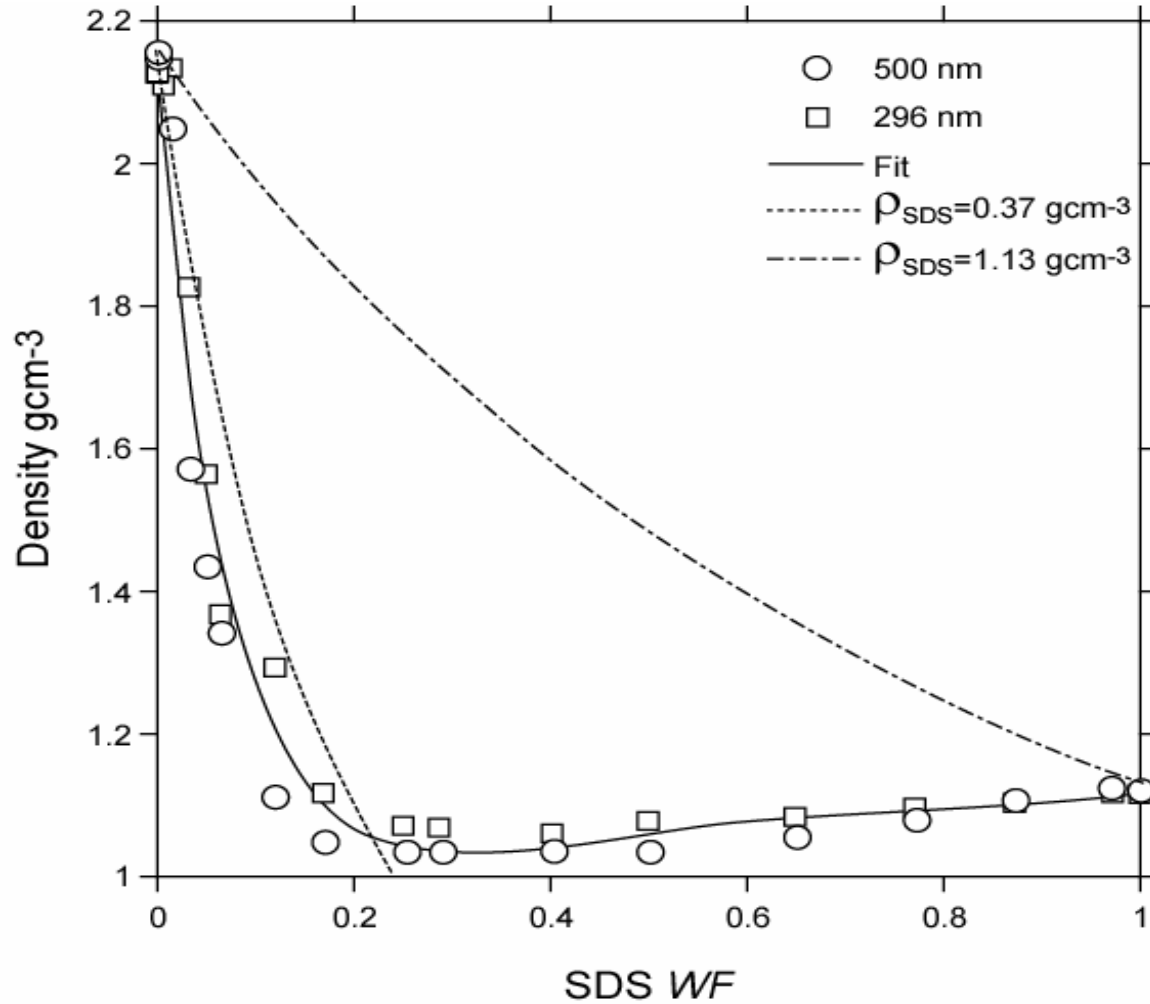
$$GF_m = \frac{d_{m,wet}}{d_{m,dry}}$$

$$GF_m = \frac{d_{m,wet}}{d_{m,dry}} = \frac{d_{ve,wet}}{d_{ve,dry} \chi_{DMA} C_c(d_{m,dry}) / C_c(d_{ve,dry})}$$

$$GF = \left(\varepsilon_O GF_O^3 + \varepsilon_{IN} GF_{IN}^3 \right)^{1/3}$$

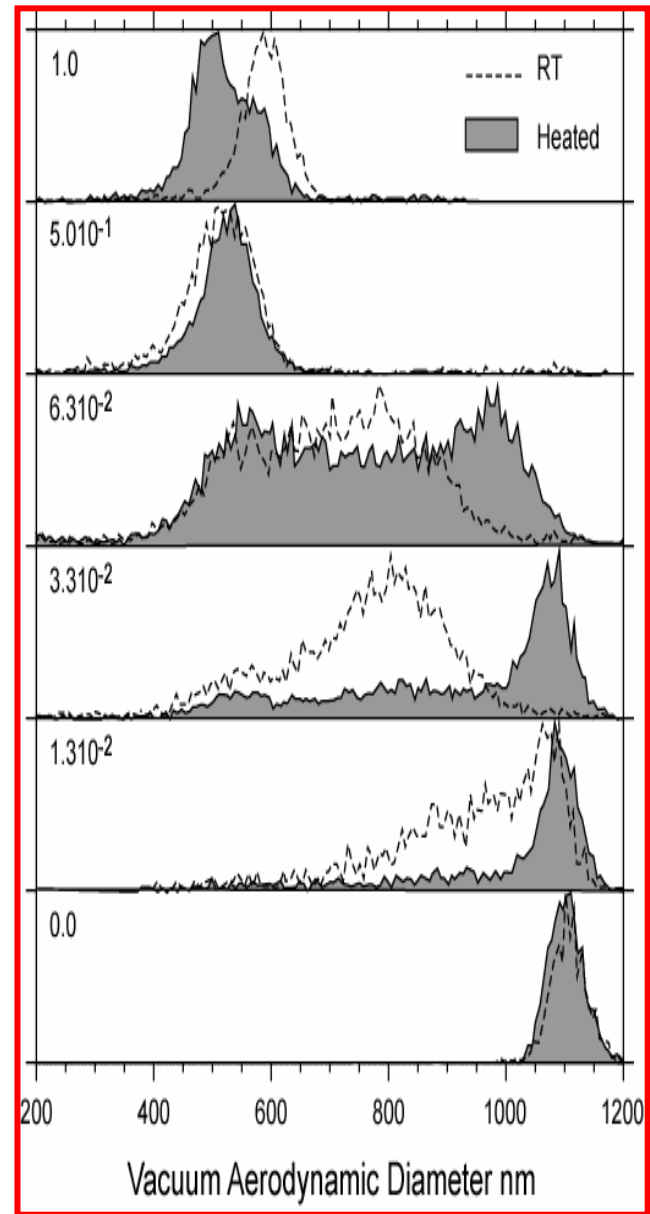
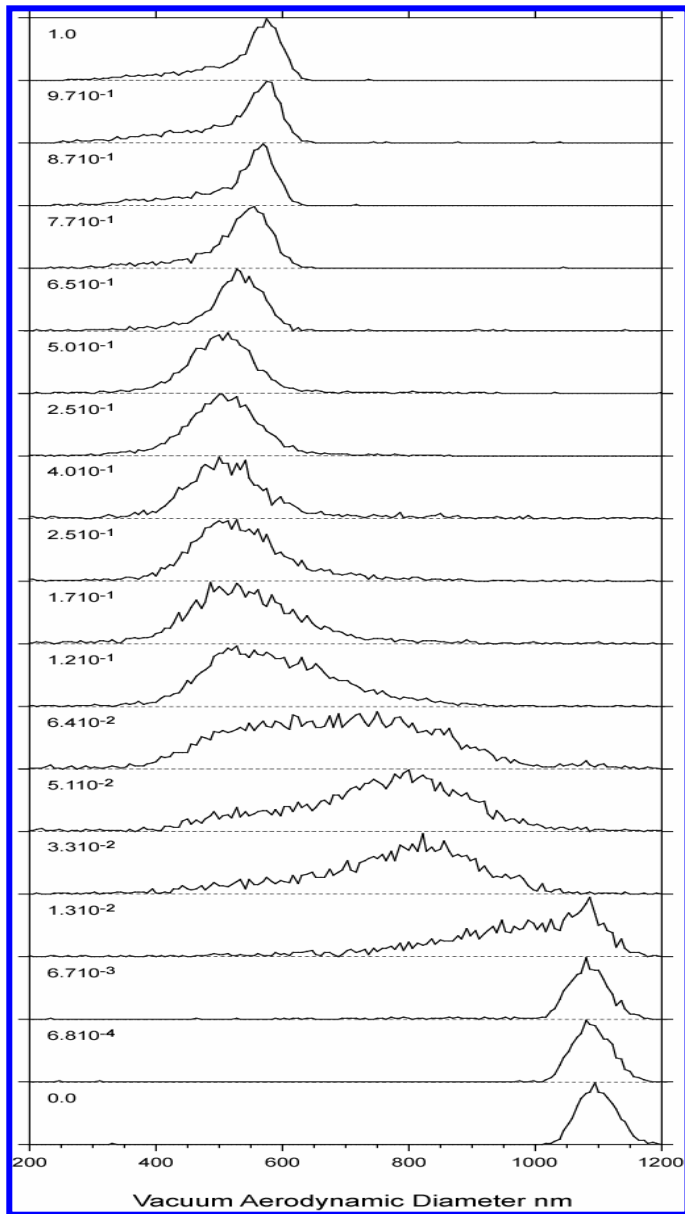
ZSR model

SN/SDS density

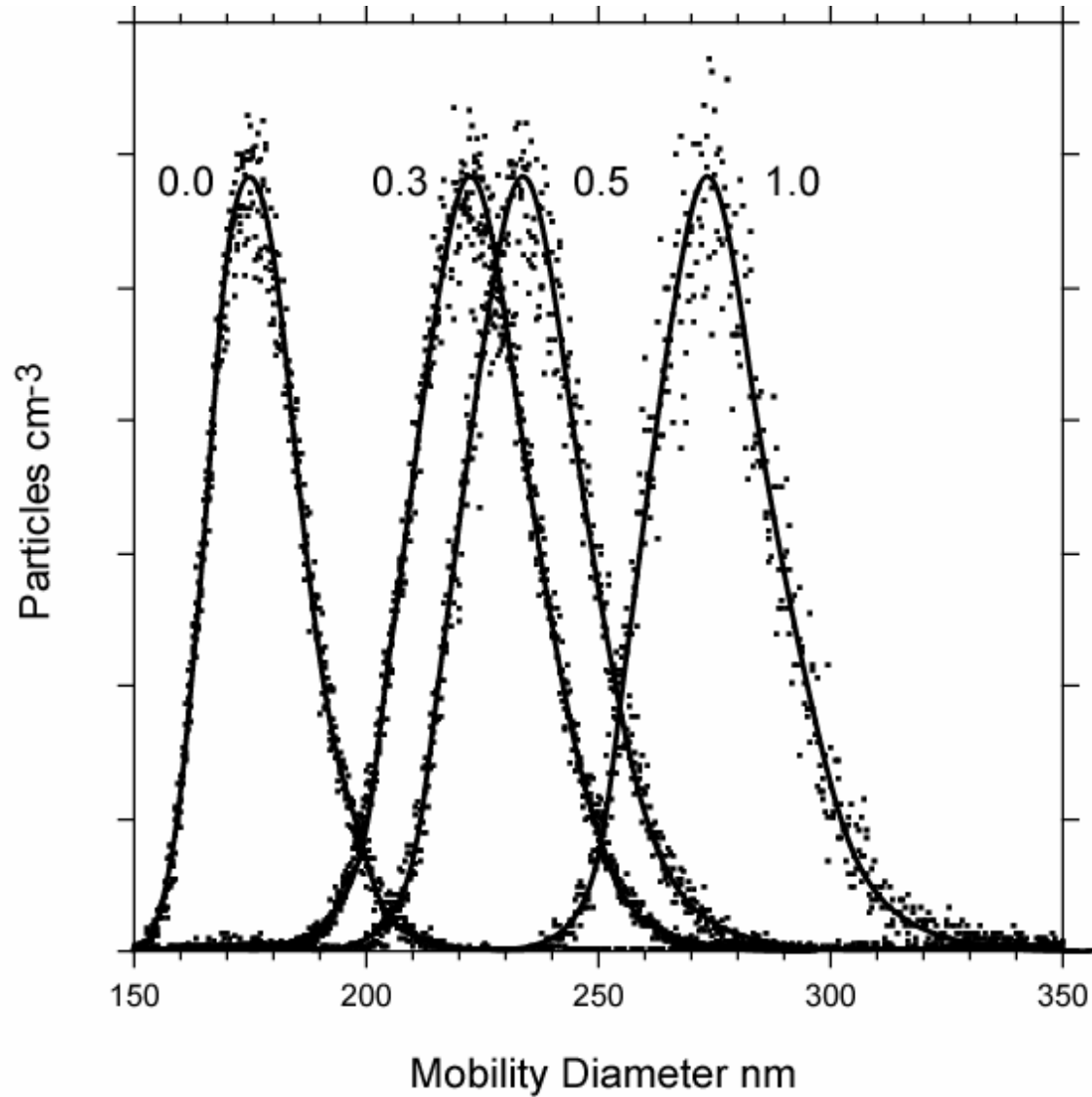


$$\rho_{SDS} = 0.24 - 3.61 \times 10^{-3} WF + 3.94 WF^2 - 5.19 WF^3 + 2.14 WF^4$$

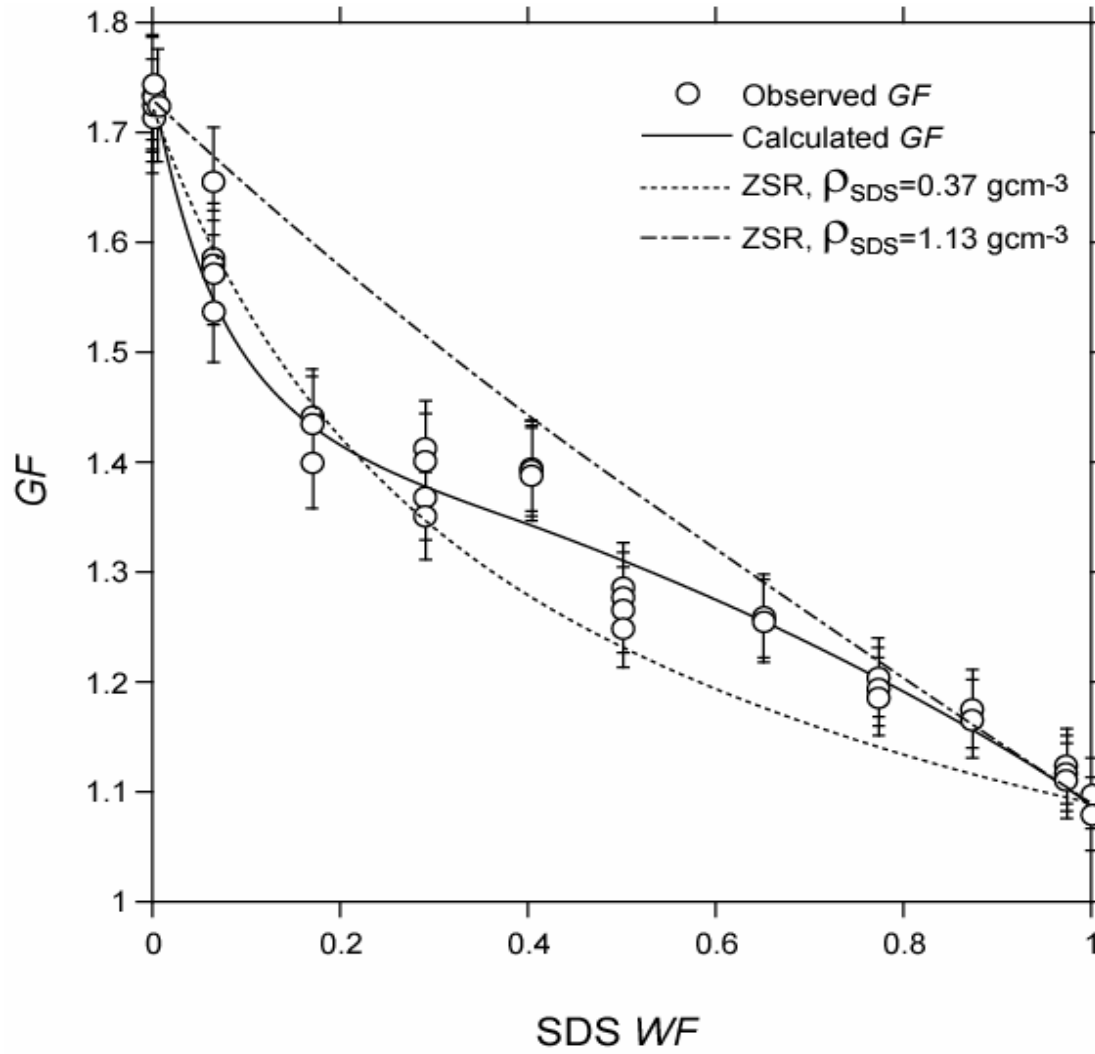
SN/SDS d_{va} distributions



SN/SDS GFs

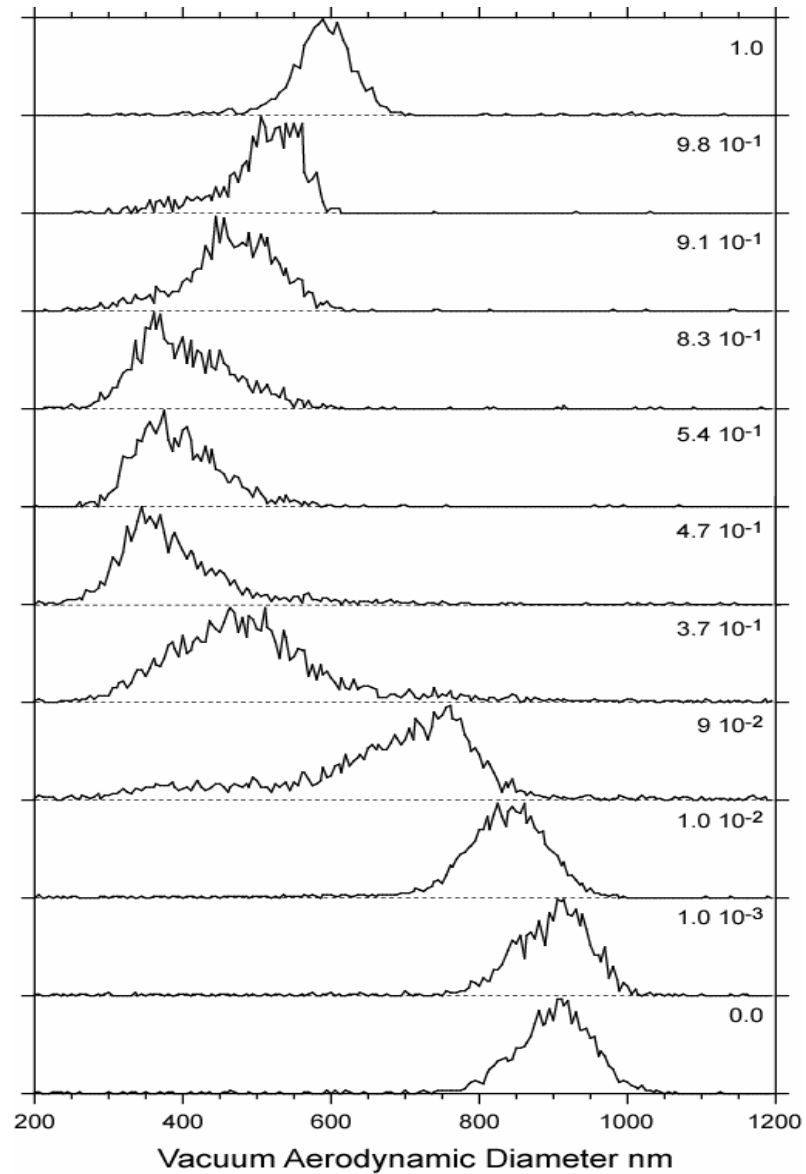


SN/SDS GFs

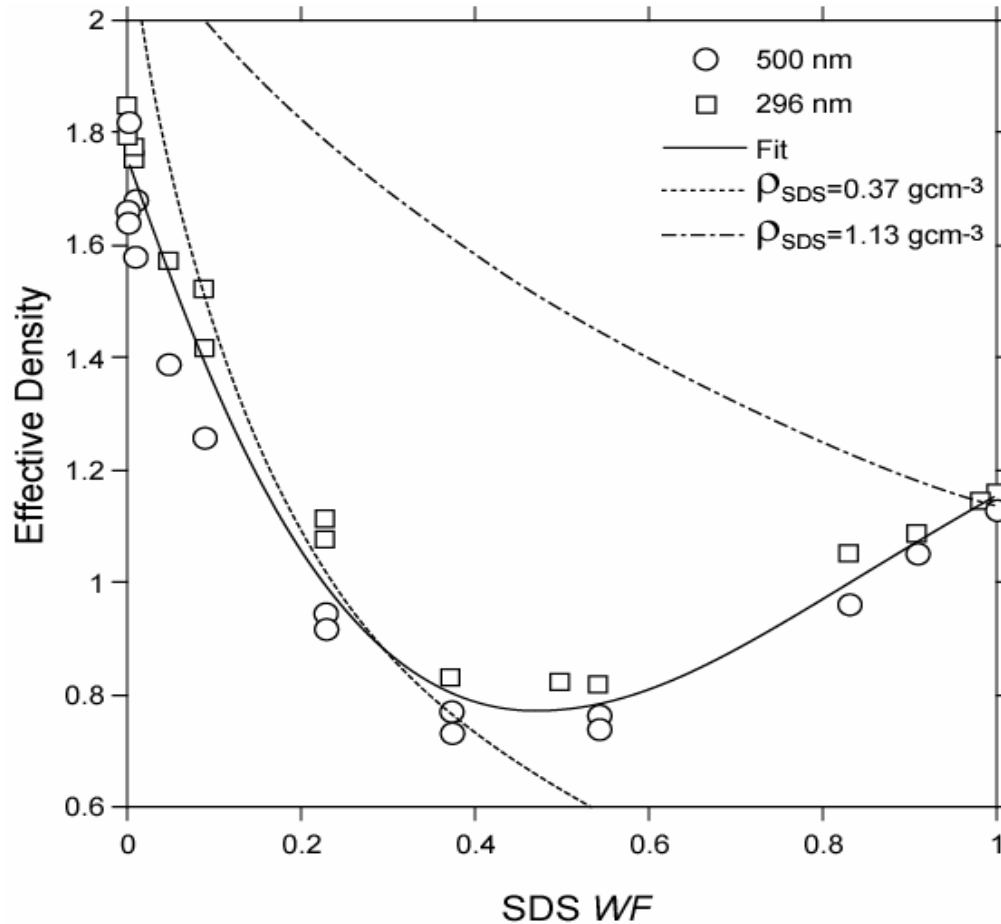


$$GF = \left(\varepsilon_O GF_O^3 + \varepsilon_{IN} GF_{IN}^3 \right)^{1/3}$$

NaCl/SDS d_{va} distributions



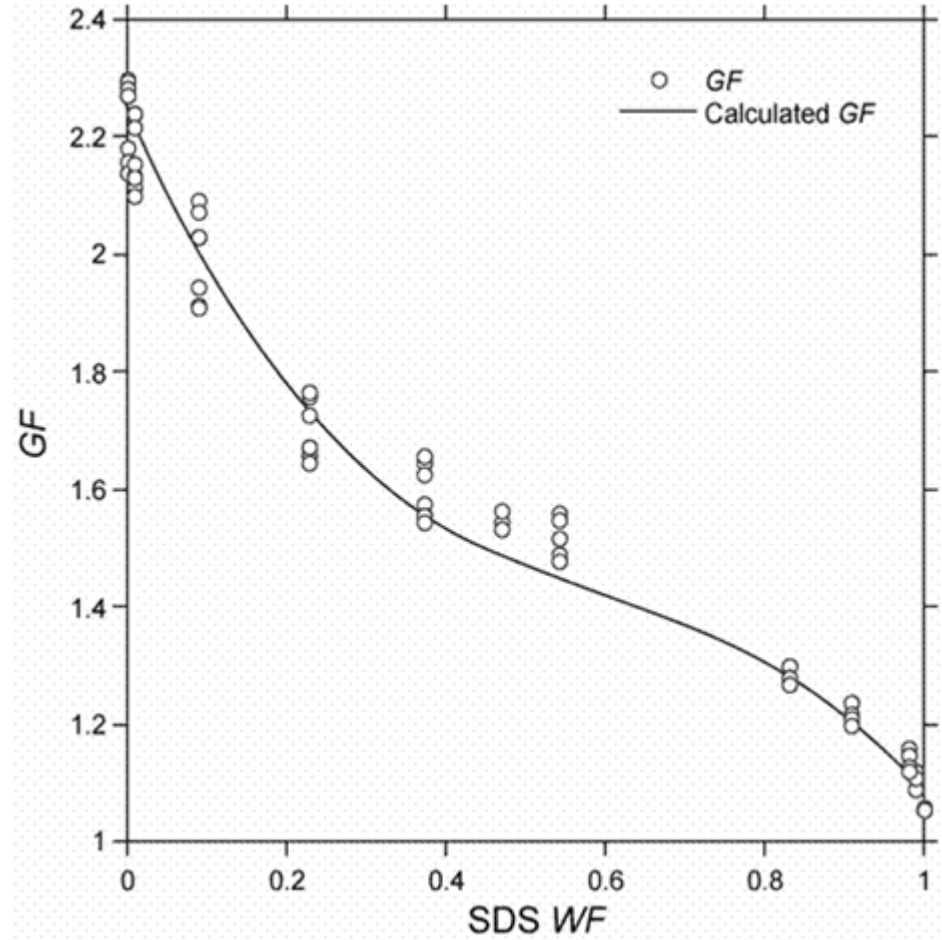
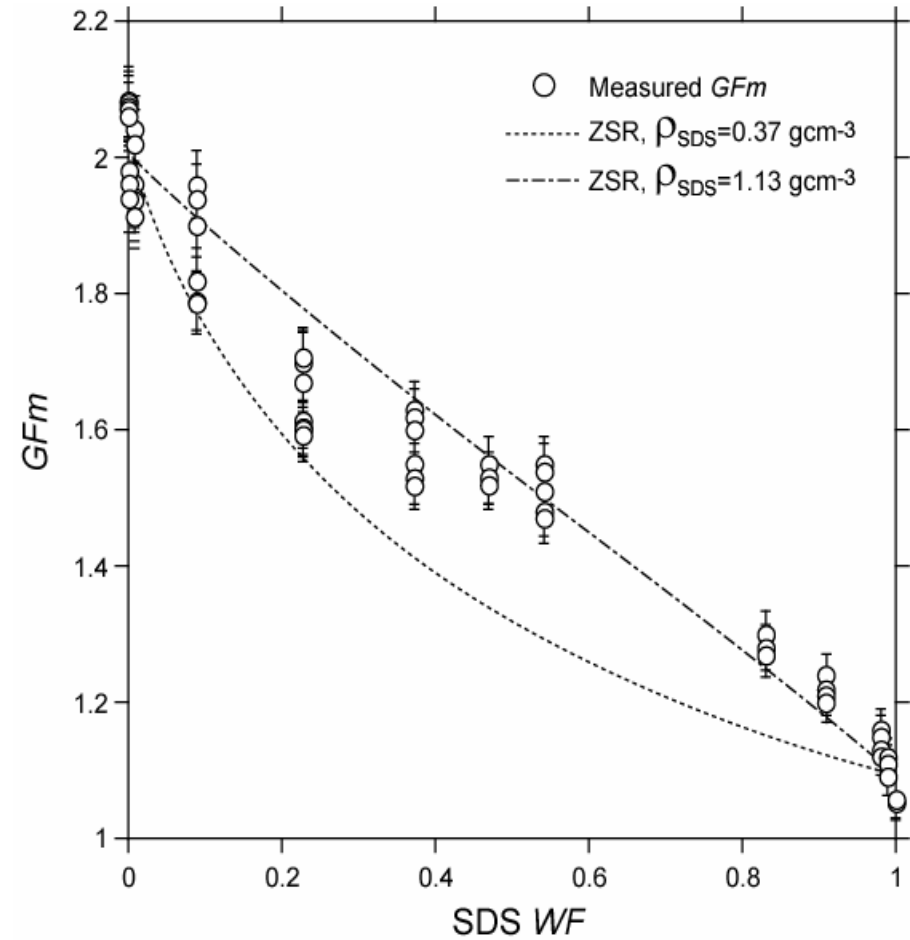
NaCl/SDS effective density



$$\rho_{SDS} = 0.381 + 0.226WF - 1.95WF^2 + 5.01WF^3 - 2.47WF^4 - 0.0554WF^5$$

$$DSF = 1.10 - 0.467WF + 0.944WF^2 - 1.09WF^3 + 0.687WF^4 - 0.181WF^5$$

NaCl/SDS GFs



$$GF_m = \frac{d_{m,wet}}{d_{m,dry}} = \frac{d_{ve,wet}}{d_{ve,dry} \chi_{\text{DMA}} C_c(d_{m,dry}) / C_c(d_{ve,dry})}$$

Conclusions

- Quantitatively described the physical properties of SN and NaCl using multidimensional analysis where independent measurements are coupled and fit.
- Behavior is complex (composition, RH, shape).
- These data (or method) could be used in prediction models and ambient sampling of organic aerosols.