Investigations of Hygroscopic Growth and Phase Transitions of Atmospheric Particles by Noncontact Atomic Force Microscopy

Antonio Checco, Susan Oatis, Derek Bruzewicz, Matthew Strasberg, Ben Ocko & Steve Schwartz
Brookhaven National Laboratory

Motivation: Improve understanding of particle deliquescence, hygroscopic growth, and “aging” pertinent to climate influence of atmospheric aerosols.

Approach: Non-contact Atomic Force Microscopy under controlled environmental conditions
Atomic Force Microscopy under controlled environmental conditions

Increasing RH (deliquescence)

Solid

NaCl

Liquid

Aqueous NaCl solution
Non-contact AFM imaging of liquids

Same setup as tapping mode but avoiding contact with the sample.

- $\nu_R = 270$ kHz
- $Q = 500$
- $A_{set} < 10$ nm

Van der Waals forces

AFM piezo-scanner

deflection sensor

dither piezo

sine-wave generator

lock-in

$\nu > \nu_R$
Environmental AFM with humidity/vapor control

Humidity is controlled within ± 2% in the range 5% < RH < 98%.

PID software control of solenoid pressure valves
Error signal provided by IC humidity sensors
Condensation of ethanol nanodrops on chemical patterns

Avoiding tip-sample contact is paramount!!

Noncontact

Tapping

liquid topography is lost (squeezing)

150nm
topography

Large phase jump denotes a transition to tapping mode

150nm
phase

Checco, Cai, Gang, Ocko, Ultramicroscopy 106, 703, 2006
Phase behavior of NaCl nanocrystals on (neutral) SiO$_2$ surface

NC-AFM profiles of NaCl crystal (height ~100-150 nm) at increasing values of RH

Salt nanocrystals are generated using an atomizer. Deposited on flat silicon oxide terminated surfaces at 65% RH.
Phase behavior of NaCl nanocristals on SiO₂ surface: preliminary results

Expected deliquescence threshold (RH=75%) for diameter > 100 nm

Additional data required to test size effect, pre-wetting and efflorescence
Synthesis of more regular and smaller crystals

- By using perfectly flat crystals it is possible to accurately measure pre-wetting.
- Crystals smaller than 50 nm are expected to deliquesce at RH value higher than that of larger crystals (curvature effect).
Prewetting of flat NaCl crystals
Study of aerosol “aging”

- Carbonaceous aerosol (organic, soot) which are initially hydrophobic are believed to become hydrophilic upon adsorption of salt or sulfuric acid from the atmosphere ("aging") and/or by oxidation.
- Examine effect of adsorbed $\text{H}_2\text{SO}_4$ or ozone exposure in modifying the wettability of prototypical organic surfaces.
Summary

- Demonstrated novel experimental approach with potential impact on environmental science.
- Validate preliminary results, demonstrate particle size effects on deliquescence/efflorescence thresholds.
- Extend to single- and multi-component aerosol particles of composition more directly relevant to ambient atmospheric aerosols.
- Initiate work on coated aerosols to simulate “aging.”