# Reversible wetting of NaCl nanoparticles at RH below deliquescence observed by environmental AFM

Derek A. Bruzewicz, Antonio Checco, Benjamin M. Ocko, Ernie R. Lewis, Robert McGraw and Stephen E. Schwartz
Brookhaven National Laboratory, Upton, NY

Atmospheric Sciences Division

Condensed Matter Physics & Materials Science

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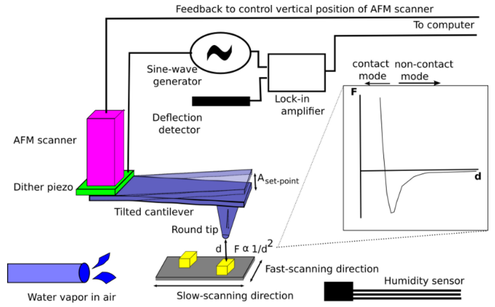
## Abstract


- The response of NaCl nanoparticles to relative humidity (RH) was characterized by measuring the height of particles deposited on a prepared hydrophobic surface with non-contact environmental atomic force microscopy (e-AFM).
- Cubic NaCl nanoparticles (35–150 nm wide) reversibly take up water with increasing RH to form a liquid-like surface layer 2–4 nm thick at RH well below the bulk deliquescence point of 75% at 20 °C. Measurable uptake begins at 70% RH.
- The maximum thickness of the layer increases with increasing RH for a given particle size, and for a given RH, increases with increasing particle size.
- The liquid-like behavior of the layer is indicated by a reversible "rounding" at the tops of the particles, where the ratio of particle height to radius of curvature increases from zero (flat top) at 68% RH to 0.7 at 74% RH.
- These observations suggest that a reorganization of mass occurs on the solid NaCl nanocrystal, and that the deliquescence of NaCl nanoparticles between 70% and 75% RH is more complex than an abrupt first-order phase transition.
- Theoretical treatments of the phase transition should account for the presence of a liquid-like layer prior to deliquescence, and for its RH-dependent thickness.

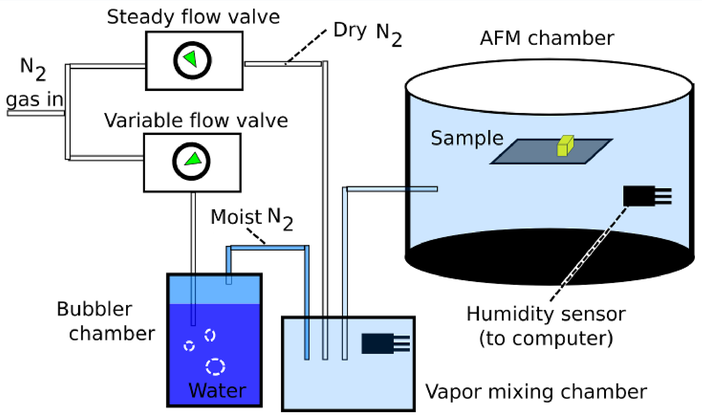

## Non-contact environmental AFM

**Nanoimaging at variable relative humidity**

- 5–10 nm gap maintained
- No transfer of material between tip and sample
- Sensitivity to changes in height of ∼1 nanometer
- 2% accuracy of RH measurement



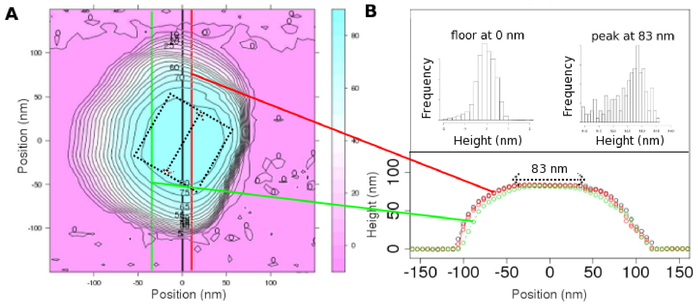

## Controlling relative humidity (RH)




Schematic diagram of the RH control mechanism

## Design and Conduct of Experiments

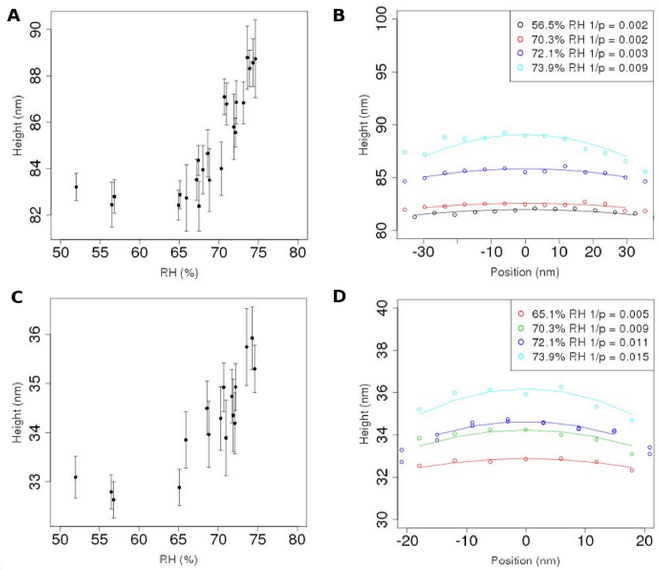
**AFM imaging and data analysis**




- Prepare moderately hydrophobic surfaces ($\angle^{water,static}_{contact} \sim 75°$)
- Synthesize cubic particles and deposit dry onto substrate
- Measure apparent height of particle relative to substrate vs. RH and position
- Correct for tip effects, especially convolution; focus on center of flat top

## Results

**Prewetting of NaCl at RH below deliquescence point**



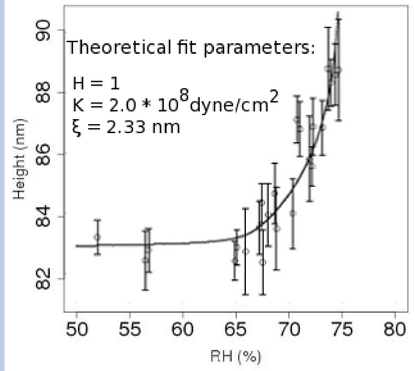

Error-bars denote standard deviation of peak height.
Points shown without error-bars are single measurements.

- Reversible formation of liquid-like layer 2–5 nm thick
- Statistically significant onset of adlayer at ∼70% RH
- Distinct rounding of initially flat tops with increasing RH

## Theory

**A model for wetting** includes:

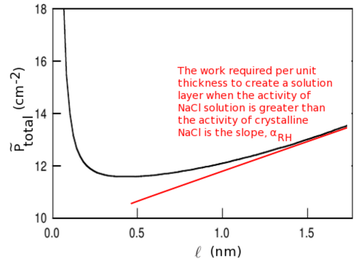
- Free-energy to form layer $\ell$ thick (1)
- van der Waals interaction (2)
- Approximation of disjoining pressure (3)




$$\tilde{P}_{capillary\ approx}(\ell) = \alpha_{RH}\ell \quad (1)$$

$$\tilde{P}_{van\ der\ Waals}(\ell) = \frac{H}{12\pi\ell^2} \quad (2)$$

$$\tilde{P}_{disjoining}(\ell) = \frac{K\xi}{kT} exp(\frac{-\ell}{\xi}) \quad (3)$$




The height $\ell$ of the equilibrium layer minimizes the total energy, $kT\tilde{P}\times$unit area, at each RH. The value used for pressure $K$ is twice that of Kuni *et al.* (1996).

## Summary and Conclusions

- e-AFM can image single nanoparticles over a range of RH, and can detect the onset of water-uptake at lower RH than is observed by polarization force microscopy or by environmental TEM.
- Reversible formation of a liquid-like layer occurs at RH below bulk deliquesence.
- The liquid-like layer can be modeled by a continuum model using parameters within a range used by other investigators. The thickness of the modeled layer is insensitive to the estimate of the layer's Hamaker constant, H.
- The presence of moisture may have implications for light scattering, and for the restructuring of atmospheric aerosol particles with morphologies that are important to Earth's radiation balance and to climate change.

## References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