

NANO HIGHLIGHT

Nanoscale Processes in the Environment: Atmospheric Nanoparticles

NSF NIRT Grant ATM 0304213

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The interaction of individual atmospheric particles with water vapor alters the physicochemical properties of these particles and therefore their effects upon climate and human health. The interaction of water vapor with particles larger than 100 nm has been studied extensively; however, knowledge of the same interaction with particles in the nanosize regime is also necessary to fully understand atmospheric processes. The deliquescence relative humidity (DRH) of particles larger than the nano-size regime is only a function of their chemical properties and not of their size. Nanoparticles, on the other hand, do not have the same behavior, as has been shown by as small number of experimental studies,^{1,2} whereas theoretical calculations among different researchers have shown diverse trends of the growth factor as a function of DRH.³⁻⁵ This limited number of experimental studies and the contradicting theoretical predictions underline the need for further experimental evidence. Examination of nanosize particles is important because they occur in high concentrations in the lower troposphere, both in polluted and pristine areas, with at present uncertain impacts on climate and human health.

Our research strategy involves the implementation of three complementary experimental methods and one theory project in the study of phase transitions of nanoparticles. One of these methods is scanning polarization force microscopy (SPFM), which is a non-contact variant of atomic force microscopy. The benefit of using the non-contact mode is the ability to use polarization forces to image the sample, thus avoiding contact with the surface or with any water that may be adsorbed to the surface. Specifically, the polarizability of a dry particle is low, while layers of water on a particle increase its polarizability. First results are shown in Figure 1 for micron-sized NaCl particles deposited on mica at 298 K.

Reconstruction (implicating increased ionic mobility) is apparent well below the crystal-to-aqueous phase transition (i.e., deliquescence), which occurs at 75% relative humidity (RH) for suspended bulk NaCl particles at 298 K. We are working to extend our studies to nanoparticles and to image their phase transitions by noncontact methods.

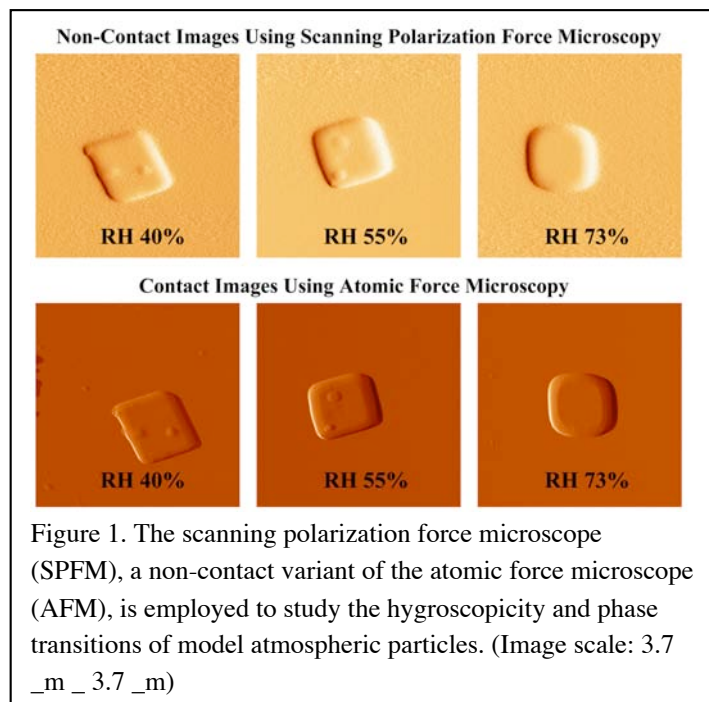
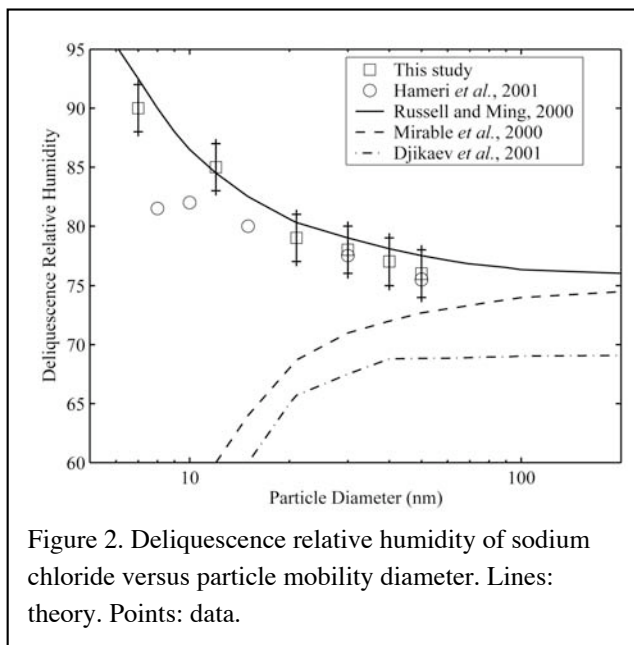


Figure 1. The scanning polarization force microscope (SPFM), a non-contact variant of the atomic force microscope (AFM), is employed to study the hygroscopicity and phase transitions of model atmospheric particles. (Image scale: 3.7 μ m \times 3.7 μ m)

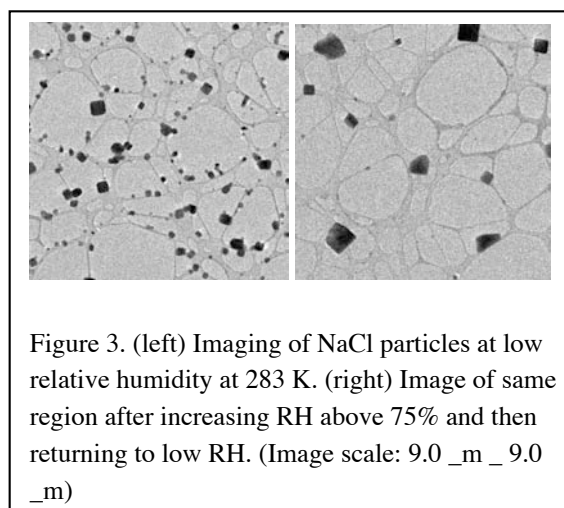
The second experimental approach, which is based upon tandem hygroscopic nano-differential mobility analyzers (DMA), has been employed to study the deliquescence of sodium chloride particles in the size range of 7-50 nm. The apparatus consists of two nano-DMAs, a nanoparticle condensation particle counter (CPC), and a series of Nafion-tube humidity exchangers. Polydisperse sodium chloride aerosol samples of low relative humidity (RH < 5%), generated by an electrospray generator, are passed through a ^{210}Po neutralizer and the first nano-DMA of the apparatus. The resulting monodisperse aerosol is then directed through the Nafion-tube humidity exchanger where its RH can be accurately adjusted. Comparing the



mean diameter of the dry to those of the hydrated samples, we are able to estimate the growth factors as a function of relative humidity for particles of different size. Figure 2 shows the measured DRH of sodium chloride nanoparticles as a function of particle size in comparison with experimental results and theoretical predictions available in the literature. Particles with diameter down to 50 nm behave similar to the larger particles, whereas the DRH of the sub-50 nm particles increases with decreasing particle diameter. The measurements agree with the experimental results of Hameri et al.¹ and corroborate the calculations by Russell and Ming⁵ that show different trends from the other two models^{3,4}. So far we have performed measurements for sodium chloride particles. Experiments now underway are investigating other chemistries and are also targeted to explore the crystallization process of inorganic solution droplets and shed some light in the hysteresis effect of atmospheric particles in the nanosize regime.

The third experimental approach is environmental transmission electron microscopy (ETEM), which to date has been used to study phase transitions of deposited NaCl particles. By increasing relative humidity (RH) and keeping temperature constant inside the environmental cell of the ETEM, deliquescence of NaCl particles has been observed and images of solution droplets have been captured. The unique benefit of the ETEM is operation at up to 8 Torr of pressure in the sample chamber, which is in contrast to the high-vacuum requirements of traditional TEM.

Figure 3 (left) shows images of NaCl particles at low relative humidity at 283 K. Figure 3 (right) shows the same region after increasing RH above 75% and then returning to low RH. Above 75% RH, the smaller particles shown in the left image deliquesce. Larger particles shown in the



right image recrystallize at low RH from an aqueous film. We are now working to extend the ETEM observations to deposited nanoparticles and to observe their transformations.

The complementary projects described above are improving our understanding of nanosize effects on atmospheric particles. Because diameter affects transport and diffusion properties, a systems-level understanding of the fate and transport of nanosize particles is incomplete without being able to predict whether a particle is in its crystalline or aqueous physical state. The implications for systems-level descriptions of nanoparticle life cycles in the environment are significant because of the strong dependence of the component processes on particle diameter.

References

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Websites

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- [2] Undergraduate summer program:
<http://www.deas.harvard.edu/nanogeosciences/>
<http://www.eduprograms.deas.harvard.edu/reu.htm#reu04>
http://www.eduprograms.deas.harvard.edu/reu_05ap.php
- [3] Principal investigator: <http://people.deas.harvard.edu/~smartin/>