Atmospheric Nanoparticles

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Critical Research Needs for Nanoparticles

- New particle formation and growth
- Particle composition and morphology
- Chemical and photochemical reactions
- Health effects
Atmospheric Nanoparticles

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Nanoparticles, which are known to strongly influence global climate, atmospheric chemistry, visibility, and the regional and global transport of pollutants and biological nutrients. Second, atmospheric nanoparticles may play critical roles in the deleterious human health effects associated with air pollution. In addition to these two well-recognized roles, nanoparticles may also significantly influence the chemistry of the atmosphere. Because their composition and reactivity can be quite different from larger particles, the presence of nanoparticles may open novel chemical transformation pathways in the atmosphere. There is possibly also an important role for nanostructures within larger particles, which often contain nanoscale features such as mineral grain agglomerates, soot spheres, or layer coatings of sulfates and nitrates. These complex morphological features likely influence a number of properties. For example, nanostructures probably affect water uptake via capillary condensation and nanoscale aqueous surface films may provide a medium for heterogeneous chemistry. In addition, nanoscale active sites on surfaces may influence particle phase transitions through heterogeneous nucleation. However, with a few notable exceptions, the potential roles and implications in atmospheric chemistry for nanoparticles and nanostructures have not been quantitatively examined.

The goal of this chapter is to provide a survey of what is currently known about nanoparticles in the atmosphere, especially in terms of their formation and growth, number concentrations and chemical composition, and chemical, physical, and mechanical properties. Although combustion sources are important sources of nanoparticles, we do not discuss the special conditions (e.g., in terms of particle dynamics) encountered in combustion plumes. This chapter complements two recent journal issues, one focused on nano- and ultrafine particles in the atmosphere (*Philosophical Transactions of the Royal Society of London A*, vol. 358, no. 1775, 2000) and the other containing papers related to nanoparticles in technology and in the atmosphere (*Journal of Aerosol Science*, vol. 29, no. 5-6, 1998). Given the mineralogy context of the volume in which this chapter appears, we also provide a general introduction to the occurrence and physicochemical properties of atmospheric particles.

At the outset of this chapter, one point of distinction is necessary regarding the term “nano” in the context of atmospheric particles. In contemporary scientific usage in many fields such as materials science, chemistry, and physics, nanoscale is understood to mean
Nano-Properties

Effect of particle diameter on deliquescence relative humidity
Hysteresis Effect: Particle Phase Depends on Relative Humidity History

\[(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}\]

**Upper Loop**
- Aqueous Particles
- Homogeneous Nucleation

**Lower Loop**
- Crystalline Particles
- Aqueous Particle
- Crystalline Particle

Relative Volume vs. Relative Humidity Graph:
- **x**-axis: Relative Humidity
- **y**-axis: Relative Volume
- **ΔG**
- **S**
- **Hysteresis Effect:** Particle Phase Depends on Relative Humidity History

\[(\text{NH}_4)_2\text{SO}_4\]
Validation of one model over another through experiment has proven difficult: the conflicting model results cite for support the same two experimental investigations on this topic.\textsuperscript{11,12} Ambiguity in the reported experimental results arises because the technique employed, which is the tandem differential mobility analyzer approach, neither directly identifies the phase of the nanoparticles nor directly measures particle diameter.

3.3.2 Proposed thermodynamic modeling

Thermodynamic models will be developed to quantify the effects of the nano-size regime on phase relations. The proposed experiments (§3.4) will provide endpoint experimental data on the size-dependence of deliquescence, hydrates, and polymorphs, and thermodynamic formulations will be developed to provide comparable model predictions that can be directly compared with experiments. Sensitivity in model output to a range of physical parameters (principally surface tensions) will be determined.

The thermodynamic model minimizes Gibbs free energy, which is formulated with the intensive properties of chemical potential ($\mu$) and surface tension ($\sigma$) in an extensive heterogeneous system of $n$ moles with surface area $a$.\textsuperscript{16} The phase change from a dry to a wet particle occurs when the Gibbs free energy of that change equals zero, i.e.,

$$
\Delta G_{\text{delq}} = \left[ \mu_S n^S + \mu_L n^L + \sigma_{LV} a^{LV} \right] - \left[ \mu_S n^S + \mu_L n^L + \mu_V n^V + \sigma_{LV} a^{LV} + \sigma_{LV} a^{LV} \right] = 0
$$

where superscripts denote the solid (S), liquid (L), and vapor (V) phases, as labeled in Figure 1.\textsuperscript{16} This approach relies on the ability of bulk thermodynamic quantities to represent the qualitative behavior of particles in the nano-size regime, which was demonstrated for the Russell and Ming model\textsuperscript{16} shown in Figure 2 for existing data.\textsuperscript{11-13} To resolve quantitative differences from experiments, we will couple this modeling technique to experimental measurements. This integrated approach means that while we use the bulk framework for predicting equilibria, shortcomings in the bulk representation of processes will be characterized as size-dependent variations that we can describe with physically consistent parameterizations. This approach provides a comparison between the expected model behavior (based on bulk interfacial tensions) of nano-size particles to experimental observations, providing a direct characterization of nano-size differences from bulk properties.

This model has been developed only for NaCl and only for DRH predictions. The first step for a comparison of $\text{DRH}_{\text{exp}}(x)$ to $\text{DRH}_{\text{model}}(x)$ for many salts will be a recalibration of the physical parameters in the model, as corresponding to the additional salts. The next step will be to extend the model to predict the RH of hydrate formation (§3.4.2) and the temperature of polymorph transition (§3.4.3). The underlying thermodynamics of a heterogeneous system characterized by $\mu$, $\sigma$, and $n$ will need only small modifications. A significant part of the model development will be extensive literature searches for values of key properties, such as $\sigma$ for the DRH work or heats of formation for the work on hydrates and
magnitude.\(^\text{85}\) To date, employing SPFM Salmeron and co-workers have successfully imaged aqueous KOH droplets (0.1 - 2 \(\mu\)m) supported on mica,\(^\text{20}\) corrosion by H\(_2\)SO\(_4\) droplets (<1 \(\mu\)m) on aluminum at variable RH,\(^\text{19}\) and the size-dependent contact angles of H\(_2\)SO\(_4\) droplets (0.2 - 1.5 \(\mu\)m) on mica.\(^\text{23}\) In studying the corrosion of Al by supported H\(_2\)SO\(_4\) droplets, Salmeron and co-workers observed the crystallization of the corrosion by-product \((\text{NH}_4)_2\text{SO}_4(\text{s})\) at reduced relative humidities.\(^\text{19}\) As part of this proposal, the instrument will be developed into a technique for the study of nanoparticles and their processes relevant to atmospheric aerosols.

Relative humidity is controlled by placing an acrylic box, which is outfitted with inlets and outlets for gas-flow, over the AFM. Proportioned humidified and dry streams of N\(_2\) flow through the box and control RH. A chilled-mirror hygrometer is employed on the outlet of the cell to measure RH. A thermistor is attached to the AFM substrate to measure \(T\). Between SPFM images, the tip can also be engaged as a normal AFM scan to determine the size and shape of crystalline particles.

### 3.3 Thermodynamic modeling of the effects of the nano-size regime on phase transitions

#### 3.3.1 Previous thermodynamic models of \(\text{DRH}(x)\)

Mirabel et al.\(^\text{14}\) provided a thermodynamic model of the effect of nano-size \(x\) on DRH, and Russell and Ming\(^\text{16}\) included more detailed physics of surface properties and hygroscopicity. According to Mirabel et al., in the nano-size regime the DRH value is predicted to decrease to much lower values than bulk systems. In contrast to Mirabel et al., the prediction of Russell and Ming is that particles having \(x < 100\) nm have increased DRH values. For instance, DRH is predicted to increase from 75% to 83% for 8 nm particles.

Russell and Ming\(^\text{16}\) point out that NaCl adsorbs multilayers of water prior to the DRH value, which is a phenomenon absent in the treatment of Mirabel et al.\(^\text{14}\) The revised Gibbs free energy for a multilayer interface includes the surface tensions of the water layer against the vapor \((\sigma^{LV})\) and of the solid crystal against the water layer \((\sigma^{SL})\) as illustrated schematically in Figure 1. A key point is that both \(\sigma^{LV}\) and \(\sigma^{SL}\) are less than \(\sigma^{SV}\). Russell and Ming show that for soluble salts that adsorb water below their deliquescence point (including NaCl), the DRH values increase with decreasing particle size for typical values of \(\sigma^{LV}\) and \(\sigma^{SL}\). This conclusion differs markedly from the formulation of Mirabel et al., where the limiting value of DRH is zero at small particle sizes. A third model for nano-deliquescence from Djikaev et al. attempts to describe the size dependent behavior by fitting a Tolman length dependence to the experimental measurements.\(^\text{15}\) The disparities among the three models are illustrated in Figure 2. The discrepancy increases radically in the nano-size range. The coated model of nanoparticle deliquescence of Russell and Ming shows that DRH increases with decreasing particle size whereas an uncoated model predicts a decrease in DRH with decreasing size.

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**Figure 1.** Schematic illustration of coated\(^\text{16}\) and uncoated\(^\text{14}\) models for nano-deliquescence. An opposite dependence of DRH on \(x\) is shown.
\[ 92 < \text{DRH}_{60\mu m} < 96\% \]

\[ \text{DRH}_{\text{bulk}} = 75.3\% @ 298 \text{ K} \]

…continue work onto other diameter particles
Nano-Structures

Effect of inclusion diameter on crystallization relative humidity
The number one source of sulfur dioxide emissions is coal burning powerplants.
TiO$_2$ Coated by Sulfate

Marine Aerosols from the Equatorial Pacific
1990 FeLINE-1 cruise

Figure 7. Transmission electron micrographs of collected Fe$_2$O$_3$ particles at different (NH$_4$)$_2$SO$_4$ loadings. Conditions: (A) 7.9 \times 10^{-3} \text{ mole/m}^3, (B) 5.2 \times 10^{-3} \text{ mole/m}^3, (C) 7.1 \times 10^{-3} \text{ mole/m}^3, (D) 6.4 \times 10^{-5} \text{ mole/m}^3. The Fe$_2$O$_3$ mode size is Dp = 400 ± 30 nm. The flow rate, the temperature gradient, and the precursor solution concentration are 2.03 SLPM, 200/20 C, and 1M, respectively.
Figure 19. Relative volume of an ammonium sulfate particle with cycles in increasing and decreasing relative humidity at 298 K. Unity volume corresponds to a nonporous, spherical crystalline ammonium sulfate particle. At 79.5% RH, deliquescence occurs and the particle spontaneously forms an aqueous spherical droplet. Upon decreasing RH, the particle remains aqueous (dashed line) until 35% RH when efflorescence occurs in chemically pure particles. Changes in volume occur from the evaporation and condensation of water vapor. A hysteresis effect is apparent because the volume on decreasing RH (the upper loop) is 125% to 200% larger than increasing RH (the lower loop) in the 35 to 79% range. In authentic atmospheric particles, crystallization can occur at higher RH values due to the presence of insoluble impurities that induce crystallization at lower supersaturations. The upper axes show the mole fraction, $x$, of the aqueous particles, saturation ratio, $S$, with respect to crystalline ammonium sulfate, and the free energy change, $\Delta G$ (kJ mol$^{-1}$), of one total mole of ammonium sulfate crystal and water vapor combining to form an aqueous solution (i.e., deliquescence). Density, curvature, and mass transfer effects are not considered.

Hysteresis Effect

Where Does Heterogeneous Nucleation Occur?

(NH₄)₂SO₄/H₂O

Upper Loop

Aqueous Particles

Crystalline Particles

Lower Loop

Homogeneous Nucleation Limit

Relative Volume

0 1 2 3 4 5

Relative Humidity

30 40 50 60 70 80 90

ΔG

0.4 0.3 0.2 0.15 0.1 0.05

S

0.5 1 2 5 10 20 30 40

-1 0 1 2 3 5 7 9

Aqueous Particle

Crystalline Particle
Dependence of Crystallization Relative Humidity of Aqueous \((\text{NH}_4)_2\text{SO}_4\) and \(\text{NH}_4\text{NO}_3\) Outer Layers as a Function of Inclusion Size

*Active site model*

\[\text{AS: } (\text{NH}_4)_2\text{SO}_4\]
\[\text{AN: } \text{NH}_4\text{NO}_3\]
\[c: \text{Corundum}\]
\[h: \text{hematite}\]

1 hr observation time

- AS DRH = 79.5%
- AS CRH = 35%
- AN DRH = 62%
- AN CRH = not observed
(110) Face of Synthetic $\alpha$-Fe$_2$O$_3$

imaged by contact under air before exposure to water or oxalate

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For 100 particles of 10-nm diameter, the maximum likelihood distribution is that 72 particles have no active sites, 23 have one site, 4 have two sites, and 1 has three or more sites.
Figure 1. Number ($\Delta N/\Delta \log D$), surface area ($\Delta S/\Delta \log D$), and volume ($\Delta V/\Delta \log D$) distributions for a typical urban aerosol. The solid lines are the size distributions, while the dashed lines show the tails between intersecting modes. The total number concentration, surface area, and volume equal the areas under the curves of each mode. From Finlayson-Pitts and Pitts (2000). Used by permission of Academic Press.

Hyytiälä 17.6.1996, 8:19 a.m.

Figure 2. Trimodal structure of the submicron particle number size distribution observed at a boreal forest in Hyytiälä, Finland on June 17, 1996, 08:09-08:19. The total particle number concentration of the submicron aerosol is 1011 particles cm$^{-3}$. From Mäkelä et al. (1997). Used by permission of the American Geophysical Union.
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