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Nanoscale Science and Technology in Soil Science

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3.1 Introduction: Nanoscience and Nanotechnology

Nanoscience and nanotechnology together represent one of the “hottest” research areas in science and engineering at the start of the twenty-first century. With new advances in instrumentation and theory, scientists have come to realize that within the range of 1 to ~100 billionths of a meter, known as the nanoscale, materials may display properties and behaviors that are unique and often cannot be described using our knowledge of either bulk systems or individual molecules. This is not necessarily a surprise to soil scientists who have known for many decades that fine-grained soil minerals such as aluminosilicate clays and ferrihydrite tend to have special properties that are distinct from those of larger minerals. The soil science community also has taken a leadership role in understanding the structures and behaviors of complex nanoscale organic matter components such as humic and fulvic acids.

Many of the natural constituents of soils are nanoparticles— for example, aluminosilicate clays, Fe(hydr)oxides such as ferrihydrite, viruses, and humic substances. Soil nanoparticles may occur as mobile colloids (Kretzschmar and Shäfer, 2005), as coatings on other mineral surfaces, and/or as mixed organic/inorganic aggregates (Nugent et al., 1998; Chorover et al., 2007). The high surface areas of nanoparticles mean that they are particularly influential in controlling the fate and transport of pollutants as well as the bioavailability of key nutrients such as phosphate and Fe (Brown and Parks, 2001; Hochella et al., 2008; Theng and Yuan, 2008). Nanoparticles interact with soil microorganisms at a profound level. Microbial processes are key to both the nucleation and dissolution of Fe and Mn (hydr) oxides (Banfield and Zhang, 2001; Fortin and Langley, 2005) and there have even been reports of biogenic uraninite nanoparticles (Bargar et al., 2008). Synthetic nanoparticles are finding their way into the environment, and how they interact within soils is a key topic of international concern and research (EPA, 2005; Nowcak and Bucheli, 2007).

Nanoparticles are important not only in soils per se but also in the broader near-earth-surface environment known as the critical zone (Hochella et al., 2008; Maurice and Hochella, 2008). Nanoparticles are ubiquitous in aquatic and marine environments, often controlling pollutant transport and nutrient bioavailability. For example, Fe oxide nanoparticles are likely to be a major source of essential Fe to ocean algae, helping to control ocean biological productivity and ultimately the global carbon cycle (Wu et al., 2001). Nanoparticles in surface waters, soils, and aquifers often control the mobilities of pollutants such as heavy metals, radionuclides, and hydrophobic organic compounds (Brown and Parks, 2001). Nanoparticles play a major role in the transport of toxic metals in acid mine drainage environments.
3.1.1 Chapter Goals

This chapter aims to describe our state-of-the-art—though rapidly changing—understanding of what makes nanomaterials unique, to provide insight into the special behaviors of nanoparticles, and to highlight how the soil science community can both benefit from and contribute to nanoscale environmental research. A key underlying principle in this chapter is that the high surface areas of nanoparticles mean that their characteristics, including stabilities and reactivities, can be extremely sensitive to surface free energy. Nanoparticles have a relatively high proportion of atoms associated with their surfaces. These surface- and near-surface atoms have different coordination environments than in analogous bulk materials. Nanoparticles may have different surface composition, different types and densities of surface sites, and different reactivities with respect to processes such as sorption, catalysis, and redox reactions (Waychunas et al., 2005). Nanoparticles also may have different overall crystalline order or structure, different stability, and unique thermal, optical, electrical tensile strength, and/or magnetic properties than observed in larger, bulk materials. We are only beginning to understand the controls on the fundamental properties of nanoparticles; how they behave in complex soil environments is even less well understood.

3.1.2 Nanoparticles and Nanominerals

A nanometer is one billionth (10⁻⁹) of a meter and the prefix “nano” is used to encompass materials and processes at this general scale. The term “nanoparticle” is used throughout this text, although its definition has been subject to much debate and continues to evolve. One common definition of a nanoparticle is any ultrafine particle that is between 1 and 100 nm in size. This size limit is sometimes applied to just two dimensions. Under this definition, various nanoparticles may or may not have properties that differ from those of larger, bulk materials. Banfield and Zhang (2001) suggested that the upper limit to the size of a nanoparticle might be defined based on the size at which fundamental properties differ from those of a corresponding bulk material. According to this definition, the maximum size range for a nanoparticle is likely to vary for different materials. Hochella et al. (2008) suggested that the size range in which particles of earth materials behave differently is often between one and at most several tens of nanometers.

Hochella et al. (2008) defined nanominerals as minerals such as ferricyanide that exist only in the nanoparticle size range, or clays that only exist with at least one nanoscale dimension. These authors defined mineral nanoparticles as minerals that are in the nano-size range, but that also exist at larger sizes. Most known minerals probably can and do exist somewhere in nature within the nanoparticle size range, although we are beginning to learn that some minerals may be differently hydrated or undergo other compositional or structural changes at small particle size so that new mineral nomenclature may need to be defined in some instances. In any case, nanominerals challenge the common definition of a mineral as “a naturally occurring homogeneous solid with a definite (but generally not fixed) chemical composition and a highly ordered atomic arrangement” (Klein and Hurlbut, 1985), because composition, structure, and especially physical properties all can change at the nanoscale.

Nanoparticles overlap in size with colloids, which range in diameter from 1 nm to 1 μm (Buffle, 2006; Figure 3.1). Nanoparticles are often included in the dissolved fraction of solution samples, as defined by passage through a 0.45 μm filter, even though nanoparticles are distinct in structure, properties, and reactivity from molecules and ions. Nanoparticles often form as secondary minerals during the weathering of larger particles, for example, kaolinite on feldspar. Such surface adhered nanoparticles can be difficult to detect and characterize by conventional means such as scanning electron microscopy (SEM) and microprobe analysis, but can potentially impact reactivity with respect to adsorption and dissolution (Nugent et al., 1998).

![FIGURE 3.1](image-url)
3.1.3 Natural and Engineered Nanoparticles

Soils are in a sense the ultimate nanoenvironments. Nanomaterials, mineral nanoparticles, and many nonmineral nanoparticles are commonly found in soils (Hochella et al., 2008; Cheng and Yuan, 2008). Viruses generally occur as nanoparticles, and bacteria may contain nanoscale features such as cilia and flagella. Microorganisms may play a role in the formation of a wide variety of nanobiominerals or biomimetic nanoparticles, such as Fe and Mn (hydr)oxides and carbonates. According to Tebo et al. (1997) microorganisms appear to be responsible for most Mn(II) oxidation in the environment, and hence they play a dominant role in the formation of Mn oxides, which primarily form as high surface area nanoparticles. The role of microorganisms in the formation of carbonate nanoparticles (Figure 3.2) is receiving a great deal of attention, particularly regarding controls on the carbonate polymorph structure, micromorphology, and microtopography (Warren et al., 2001). Humic substances tend to occur within the nanoscale size range (Figure 3.3; Maurice and Namjesnik-Dejanovic, 1999; Namjesnik-Dejanovic and Maurice, 2001), and their composition, structure, properties and behaviors have long challenged the environmental geochemistry/soil chemistry communities. Black carbon, which forms from the incomplete combustion of fossil fuels, may occur in the nanoscale size range or larger, and is present in many soil environments (Hedges et al., 2000). Given that black carbon tends to be highly unreactive with respect to oxidation, it may represent an important sink of carbon in the global carbon cycle (Kuhlbusch and Crutzen, 1995).

Engineered nanoparticles are becoming increasingly widespread in the environment, and their potential impact on soil and plants is only beginning to be considered (e.g., Nowack and Bucheli, 2007). The U.S. Environmental Protection Agency (EPA, 2005) describes four categories of intentionally manufactured nanoparticles. These are: carbon-based materials such as the fullerenes and carbon nanotubes; metal-based materials such as quantum dots and nano-silver along with reactive metal oxides such as zinc oxide (ZnO) and titanium dioxide (TiO2); dendrimers, which are nanopolymers constructed of branched units; and nanocomposites. Nanoparticles also may be manufactured unintentionally as a result of grinding, combustion, and other processes.

Gold nanoparticles were used in medieval times in stained glass window production. Nanoparticulate (3.5–100 nm) gold suspensions in water create an intense red color due to plasmon absorption (Brust and Kiely, 2002). Nanoparticulate gold has become the subject of broad industrial interest due to strong catalytic capabilities (Brust and Kiely, 2002). Thiol-stabilized gold nanoparticles may self-assemble into superlattices (Giersig and Mulvaney, 1993) whose change in conductivity in the presence of different organic vapors has led to the development of novel gas sensors (Wohltjen and Snow, 1998). Silver nanoparticles are being widely used as bactericides (Brust and Kiely, 2002). TiO2 nanoparticles are used in a wide array of applications, including heterogeneous catalysis, photocatalysis, in solar cells for the production of hydrogen and electric energy, gas sensing, pigmentation (paints and cosmetics), sunscreen, protective coatings, and electronics applications (Diebold, 2003).

Discovery, characterization (Kroto et al., 1985), and eventual engineering of fullerenes helped to ignite the nanotechnology revolution. Like many nanomaterials, the definition of the word “fullerene” is subject to some debate and is evolving. Fullerenes are allotropes of carbon, the most famous of which, Buckminsterfullerene, has the formula C60 and is about 1 nm in diameter (Figure 3.4). Fullerenes can occur naturally, and have been found in C-rich metamorphic rocks known as shungite.
and behaviors of nanoparticles versus ions and molecules or larger, bulk-scale materials, so that the nanoscale represents a true frontier for revolutionary research in science and engineering.

Much of our past understanding of the properties and behaviors of small particles developed over many decades through traditional approaches in (surface) chemistry and physics. Yet, through recent developments in new nanoscale techniques and approaches, we are learning that many nanoparticles and nanoscale processes do not conform to long-held theories and conceptions. In this section, we compare and contrast classical theories and approaches of size, stability, and reactivity with our new and evolving nanoscale understanding.

3.2 Nanoparticle Size and Structure

The classical means of determining the structure of a crystalline material is by x-ray diffraction (XRD) as part of x-ray crystallography. Based on a diffraction pattern, the crystallographer can determine detailed information about the mean positions of atoms in a crystal, chemical bonds, and degree of disorder. However, single-crystal XRD, which is the best method for determining structure, is not feasible for nanoparticles because of their small size.

Although it can be difficult to determine nanoparticle structure by classical XRD alone, a number of other techniques can be helpful, particularly when applied in combination. High-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) can help in determining whether particles are crystalline or amorphous. The TEM image in Figure 3.5 shows ~10 nm diameter hematite nanoparticles with lattice fringes indicating an ordered crystalline structure.

Other techniques that can be helpful for determining the structure and/or composition of nanoparticles include synchrotron-based x-ray absorption spectroscopy (XAS) and x-ray scattering methods coupled with pair distribution function (PDF) analysis. PDF can allow for determination of changes in interatomic distance as a function of radius, composition, and other behaviors of nanoparticles versus ions and molecules or larger, bulk-scale materials, so that the nanoscale represents a true frontier for revolutionary research in science and engineering.

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Nanoscale Science and Technology in Soil Science

For decades, soil scientists and mineralogists have pursued the structure of the Fe hydroxide nanomericial ferrihydrite. Ferrihydrite generally occurs as particles <10 nm, although often aggregated, is poorly ordered, and can have variable structural order. Ferrihydrite is generally designated 2-line or 6-line depending upon the number of reflections that appear in x-ray diffractograms as order increases. Ferrihydrite is not only of interest to the environmental community but also to the biomedical community. This is because ferrihydrite forms the core of the important Fe storage protein, ferritin (Pan et al., 2009). Hence, there is tremendous interest by the broad scientific community in determining the structure of ferrihydrite.

Recently, Michel et al. (2007a, 2007b) suggested that ferrihydrite nanoparticles 6–2 nm in size all have the same composition (Fe₃O₄(OH)₂) and structure described by the hexagonal space group P6₃mc. As particle size decreases from 6 to 2 nm, there is evidence of increasing disorder and distortion of some sites. Michel et al. (2007a, 2007b) showed that for 6 nm particles, the hexagonal unit cell dimensions \( a \approx 5.95 \) Å and \( c \approx 9.06 \) Å and the structure contains 20% tetrahedrally and 80% octahedrally coordinated Fe. For 2 nm particles, the hexagonal unit cell dimensions decrease slightly and some of the Fe sites have lesser site occupancy or show evidence of distortion. This model has proven to be controversial and perhaps at least partly incorrect (Rancourt and Meunier, 2008), demonstrating how difficult it can be to determine definitively the structure of nanoparticles of interest to the soil community.

Another common application of XRD has been determination of particle size. Application of the Scherrer equation to observed peak (or line) broadening in XRD patterns has been used to determine particle size for particles up to about 0.1 μm. However, the Scherrer equation often cannot be applied reliably to nanoparticles because of issues such as the fact that a large number of atoms in nanoparticles are associated with the surfaces of particles and aggregates, which limits translational symmetry (Hall et al., 2000). New approaches, for example, based on using the Fourier transform of a Debye–Scherrer diffraction pattern, can often provide information on average particle dimensions (Hall et al., 2000). The Fourier method can be used even when only a limited range of scattering angles has been measured. When details of particle size distributions rather than simply average particle sizes are needed, other techniques such as TEM imaging and small-angle x-ray scattering (Glatter and Krathy, 1982) can prove invaluable. PDF analysis applied to x-ray scattering results can be used to define particle size for nanoparticles of only a few nanometers in size, if shape effects are considered (Kodama et al., 2006). Michel et al. (2007b) found good agreement between results of PDF analysis and TEM-based measurements of particle size for different ferrihydrite samples. Nanoparticle aggregation is common and can complicate nanoparticle size determinations. In such cases, it can be useful to report both apparent individual particle size distributions and aggregate size distributions based on TEM observations.

Detecting and determining the structure and composition of nanoparticles adhered to the surfaces of larger minerals or rocks can be even more challenging. For example, Nugent et al. (1998) observed a patchy coating of nanoscale crystalline and amorphous aluminosilicate material onfeldspar that had been naturally weathered in a spodosol. The coating was “largely undetected under scanning electron microscopy” but readily apparent in atomic force microscopy (AFM) images. Composition was determined from results of x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and secondary ion mass spectrometry (SIMS) analysis. Recently, Livi et al. (2009) characterized nanoscale mixed Ni-Al hydroxide surface precipitates on the clay mineral pyrophyllite using analytical electron microscopy, HRTEM, selected-area electron diffraction (SAED), powder XRD, and x-ray absorption fine structure (EXAFS) spectroscopy. The authors stressed the importance of applying such a combination of state-of-the-art techniques to analyze nanoscale surface precipitates.

### 3.2.2 Nanoparticle Surface Area

The world of nanoparticles is fundamentally a world of surfaces. Nanoparticles have extremely high specific surface areas for their volume and a significant proportion of atoms associated with nanoparticles occur at surfaces. For example, if we were to take a cube 1 mm on a side and divided it into cubes 1 nm on a side, the total volume would remain the same. But, the surface area would increase a million fold.

For a spherical particle, the ratio of surface area (in \( \text{nm}^2; A = 4\pi r^2 \)) to volume (in \( \text{nm}^3; V = 4/3\pi r^3 \)) is inversely proportional to the particle radius \( r \) (in nm) according to the simple relationship:

\[
\frac{A}{V} = \frac{3}{r}
\]

(3.1)

As a particle becomes smaller, its surface area becomes an increasingly larger component of its overall form or structure.

### 3.2.3 The Concept of Surface Free Energy

The significance of surface area in environmental systems is readily apparent from the simple experiment of pouring a little oil into water. The oil immediately balls up into spheres (or flattened spheres at the water surface). The hydrophobic oil is taking on the shape that minimizes the surface area in direct contact with water. This and other related commonplace observations suggest that surfaces must have some energy associated with them, known as the surface free energy (or, more correctly in many circumstances, the interfacial free energy). Surface free energy is a driving force for many physical or chemical transformations that act to minimize the surface free energy.

When new surface area is formed, the associated change in surface free energy must be considered in the overall energy change of the system. The (specific) surface or interfacial free energy \( \gamma \) is defined as:

\[
\gamma = \left( \frac{\delta G}{\delta A} \right)_{p,T}
\]

(pressure, temp., remain constant)  (3.2)
where

\[ G \] is the Gibbs free energy (in kJ)

\[ A \] is the surface area (in m²)

An interface will only be stable if the free energy of formation of the interface is positive; otherwise, the interface would eventually disappear. It should be noted that surface free energy refers to the excess free energy that molecules or atoms have by virtue of their being associated with a surface.

For a system that contains a surface, the total free energy of the system is the sum of the bulk free energy (\( G_{\text{bulk}} \)), which in turn is the sum of the molar free energies of formation of its constituents, \( i \), \( \Sigma \mu_i n_i \), where the chemical potential \( \mu = (\delta G/\delta n_i)_{T,P} \), plus the total excess free energy of formation of all surfaces and interfaces \( j (G) \). The surface (or interfacial) free energy is given by \( \Sigma \gamma_i A_j \). The total free energy (in kJ) is thus

\[
G_{\text{tot}} = G_{\text{bulk}} + G_{\text{surf}} = \Sigma \mu_i n_i + \Sigma \gamma_i A_j
\]  

(3.3)

(3.4)

This concept of surface free energy has important implications for many environmental processes, especially those involving small particles with high specific surface area. A summarizing principle is that for small nanoparticles that have high specific surface area, anything that affects surface free energy can affect overall nanoparticle stability.

### 3.2.4 Surface Free Energy and Classical Mineral Nucleation Theory

Surface free energy plays an important role in mineral nucleation. Homogeneous nucleation of a new mineral phase from solution necessarily passes through a step in which a nanoparticle forms with very high specific surface area. The free energy of nucleation of a single crystal (\( \Delta G_n \)) is the sum of the change in bulk free energy (\( \Delta G_{\text{bulk}} \)) and the change in free energy that occurs upon formation of a new interface (\( \Delta G_{\text{interf}} \)) (Berner, 1980):

\[
\Delta G_n = \Delta G_{\text{bulk}} + \Delta G_{\text{interf}}
\]  

(3.5)

where \( \Delta G \) values are in kJ mol\(^{-1} \).

For a spherical particle,

\[
\Delta G_n = -\left( \frac{4}{V} \right) \pi r^3 k_B T \ln(\Omega) + 4\pi r^2 \gamma
\]  

(3.6)

where

\[ V \] is the molecular volume of the precipitate (m³)

\[ r \] is the radius of the nucleus (m)

\( k_B \) is Boltzmann’s constant (1.3806 × 10\(^{-23} \) kJ K\(^{-1} \))

\( \Omega \) is the saturation ratio

\( T \) is the temperature (K)

\( \gamma \) is the surface free energy per unit surface area of the nuclei (kJ m\(^{-2} \))

When the solution is supersaturated, \( \Omega > 1 \). \( \Delta G_n \) has a maximum at the critical size of the nucleating crystal, which is designated \( r^* \), or the critical nucleus. Once the critical nucleus is formed, any additional growth of the crystal results in a decrease in free energy and the overall process transitions from one of nucleation to growth. At any specific value of \( \Omega \), particles with \( r > r^* \) will tend to grow and particles with \( r < r^* \) will tend to dissolve. Greater \( \Omega \) corresponds to smaller critical nucleus size, that is, smaller nuclei will be stable in more highly supersaturated solutions.

This element of classical nucleation theory has important implications for the mechanisms of mineral nucleation (Figure 3.6; Lower et al., 1998a, 1998b). At high supersaturation, we can expect that minerals will be likely to nucleate homogeneously in solution. But, at low supersaturation, such homogeneous nucleation is far less likely and heterogeneous nucleation on already existing surfaces (if such are available) is more favorable and thus more likely to occur. Soil environments, which tend not to be highly supersaturated with respect to many mineral phases, should not undergo much if any homogeneous nucleation directly from solution leading to crystal growth, although heterogeneous nucleation on the surfaces of already existing particles can occur more readily. An example of heterogeneous nucleation could potentially be formation of kaolinite as a secondary mineral precipitate on feldspar, although it should be emphasized that we do not fully understand the mechanisms of kaolinite secondary mineral formation in different environments.
3.2.5 Particle Size and Stability: Classical Theory

Related to this view of particle size and nucleation theory, we can consider how particle size affects stability. The high specific surface areas of small particles has always been taken to indicate that particles become less stable with decreasing size so that nanoparticles should, for the most part, be unstable. To understand the phenomenon of stability relationship to size, we can begin by considering how the pressure within a bubble changes with bubble size (or radius of curvature). According to the Young–Laplace equation, the pressure difference ($\Delta P$) on either side of the surface of a thin film is related to the surface or interfacial tension ($\gamma$) and the radii of curvature ($R_s, R_y$) in m of the surface:

$$\Delta P = \gamma \left( \frac{1}{R_s} + \frac{1}{R_y} \right)$$  \hspace{1cm} (3.7)

For a spherical bubble, $R_s = R_y$, and the Young–Laplace equation reduces to

$$\Delta P = \frac{2\gamma}{R}$$  \hspace{1cm} (3.8)

Thus, the pressure inside a bubble becomes increasingly large as the bubble size decreases. Very small bubbles thus tend to be unstable, and initial bubble formation requires energy to overcome this free energy nucleation barrier.

Expanding this concept from gas bubbles in solution to more general interface phenomena, changes in particle stability with size are traditionally described by the modified Kelvin equation. This equation states that as a hypothetical particle gets smaller in size ($r$, in m) through the nanoscale range, its solubility ($s$) increases exponentially:

$$\frac{s(r)}{s_\infty} = \exp \left( \frac{2\gamma V_D}{rRT} \right)$$  \hspace{1cm} (3.9)

where
- $\gamma$ is the surface energy
- $V_D$ is the molar volume of the disperse phase ($m^3$)
- $R$ is the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
- $T$ is the temperature (K)

The term $s_\infty$ refers to the solubility of a hypothetical particle with an infinite planar surface, that is, in the absence of curvature.

The marked decrease in stability with decreasing particle size can lead in some systems to evolution in particle size over time. Consider an aqueous system in which many small crystals have formed from a highly supersaturated solution. The numerous small crystals together have very high combined, total surface area. This system of small, high specific surface area particles is thermodynamically unfavorable relative to a system with fewer large crystals and therefore lower interfacial free energy. Some of the small crystals will dissolve while others grow at their expense to larger dimensions. This spontaneous process of increase in average particle size over time is known as Ostwald ripening, named after Wilhelm Ostwald who first described the process in 1896. Because a system with many small particles has a larger overall surface area-to-volume (or mass) ratio than a system of few large particles, Ostwald ripening minimizes the total free energy of the system by decreasing surface (interfacial) energy.

The above discussion of classical theory suggests that nanoparticles in aqueous environments should be highly unstable and should eventually evolve into larger and more stable crystals. Yet, many nanoparticles can remain stable for long periods of time in aqueous suspensions or in porous media. As we shall see in the section below, particle size and stability can be related in a complex manner at the nanoscale, and classical theories do not always provide good explanations for observed phenomena.

3.2.6 Nanoparticle Stability: When More Than Size Alone Matters

Classical theories of crystal nucleation, growth, and stability as related to particle size withstood decades of inspection, helping to explain many important phenomena in the field and the laboratory. Within the last few years, however, nanoscience is demonstrating that the classical approaches do not always provide a clear understanding of phenomena involving minerals and other natural solids at the nanoscale. Conceptually, soil scientists recognize the general problem immediately: if small particles are inherently unstable, then why are soils, even paleosols, often dominated by mineral or amorphous solid particles less than 1 μm in diameter, including nanoparticles? Is it just that the kinetics of growth are very slow in low-temperature environments? Or, are there thermodynamic controls; that is, can nanoparticles be thermodynamically stable for reasons that we do not yet fully understand? These are questions that we do not yet have answers for in many systems. However, the work of researchers such as Navrotsky and her colleagues (Navrotsky, 2001, 2003; Navrotsky et al., 2008) is starting to suggest that both kinetics and thermodynamics can play a role in nanoparticle longevity in both the lab and the field.

In order to determine the controls on mineral nanoparticle stability as a function of size, one would ideally like to be able to grow nanoparticles of a given mineral phase in which only the size changes, but not the structure or composition. However, for many phases, it is impossible to change size, at least for the smallest nanoparticles, without also changing structure and/or hydration (Navrotsky et al., 2008). Among other factors, very small nanoparticles, in the 1–10 nm size range, have a high proportion of total atoms at or very near the surface. These atoms...
experience different bonding environments than atoms of the same mineral in the bulk of a larger crystal. Thus, for very small mineral nanoparticles, the high proportion of surface and near-surface atoms can make it virtually impossible to change size independently of structure, and for many minerals, of composition. Moreover, very small nanoparticles of minerals such as hematite often are more hydrated than larger crystals, and this again affects stability (Navrotsky et al., 2008).

Difficulties associated with determining the structures of nanoparticles were discussed in Section 3.2.1. Beyond the overall structure of nanoparticles, we often cannot determine the surface structure and microtopography of mineral nanoparticles; yet, both of these characteristics affect surface free energy and crystal stability, especially within the nanoparticle size range. It can also be difficult to discern the ratios of different crystallographic faces exposed at the surfaces of nanoparticles. Given that different faces may have different structures, reactivities, and surface free energies, this further complicates our understanding of how stability changes as a function of nanoparticle size (A. Navrotsky, University of California at Davis, personal communication). Finally, impurities tend to accumulate at the surfaces of particles, and impurities can thus be expected to play a particularly important role in nanoparticle stability and reactivity (Waychunas et al., 2005).

Recall from above that total free energy of a particle is equal to the sum of bulk free energy plus surface/interfacial free energy,

\[
G_{\text{tot}} = \sum \mu_i n_i + \sum \gamma_j A_j
\]

(3.4)

The surface/interfacial free energy may become a major and potentially even dominant component of \(G_{\text{tot}}\) for nanoparticles, especially in the size range of only a few nanometers in diameter. This means that nanoparticle stability is not just a function of size, alone, but rather of complex structural, compositional, and microtopographic characteristics of the surface/interface.

Navrotsky’s group has shown that the different polymorphs of the oxides of Al, Fe, Ti, and Zr can show varying degrees of stability at different particle sizes in the nanoscale versus micron scale (Navrotsky, 2001, 2003; Navrotsky et al., 2008), related to a large extent to differences in surface free energy. Phases that are metastable as micron-scale or “bulk” materials generally have larger surface energies than other polymorphs that are slightly metastable as bulk materials. Because of this competition between bulk metastability and surface energy, nanoparticulate oxides can exist as different stable polymorphs at different size ranges. This process can lead to crossovers in stabilities of different phases as a function of particle size.

Navrotsky et al. (2008) found that stability crossovers can be different for hydrated versus anhydrous surfaces of the Fe(hyd) oxide system. For example, particle size and hydration can play a key role in determining the relative stabilities of hematite and goethite of different nanoparticle sizes (Navrotsky et al., 2008). Surface enthalpy and free energy are generally much higher for anhydrous oxides such as hematite than for oxyhydroxides such as goethite. The lower surface enthalpy/energy for the hydroxide phase goethite allows this mineral to be stabilized relative to the oxide hematite at \(<60\) nm, corresponding to high surface area. Although micron-scale hematite particles in water tend to be more stable than goethite, the nanoparticle size range tends to favor goethite stability (Figure 3.7). The equilibrium relationships between hematite and goethite nanoparticles are sensitive to variations in other factors such as temperature, the activity of water, and Al substitution. Given that impurities tend to associate with surfaces, the high surface areas of nanoparticles may lead to the impurities being a significant proportion of the overall atoms associated with a nanoparticle, so that impurities can be expected to be particularly important to nanoparticle stability.

3.2.7 Stability and the Medium Surrounding a Nanoparticle

Another factor that can strongly impact nanoparticle stability in soils and other porous media is the solution composition, including pH, ionic strength, and concentrations of potential
sorbates, in which nanoparticles are found. Because of the small size of nanoparticles and the high specific surface area, materials such as cations, anions, and organic molecules adsorbed to nanoparticles can become a major component of the overall nanoparticle structure and composition. This means that sorbed materials can affect nanoparticle stability, especially for nanoparticles less than a few nanometers in diameter. Because pH affects nanoparticle oxide surface site protonation, pH can affect stability through its effects on surface free energy, alone, beyond considerations of bulk saturation state.

3.2.8 A New Concept of Mineral Growth from Nanoparticles: Oriented Attachment

While Ostwald ripening appears to occur in many systems (Lower et al., 1998a, 1998b), minerals may grow from nanoparticulate nuclei by another mechanism known as oriented attachment. Oriented attachment as a mechanism for dislocation generation in otherwise defect-free nanocrystals has been demonstrated through the work of Banfield and her colleagues (Penn and Banfield, 1998a, 1998b). Oriented attachment is a process whereby adjacent nanoparticles spontaneously self-organize so that they share a common crystallographic orientation. The oriented particles are then joined along a planar interface, decreasing the overall surface area and surface free energy. Oriented attachment also can be a mechanism for dislocation generation in otherwise defect-free nanocrystals, when there is a small misorientation at the interface between the joining nanoparticles (Penn and Banfield, 1998b). Oriented attachment may also result in crystals that are separated by twin boundaries or other planar defects (Penn and Banfield, 1998b); the twin boundaries sometimes have atomic arrangements that are distinct from the crystal components on either side of the boundary (Figure 3.8; Penn and Banfield, 1998b). An important question is how prevalent oriented attachment is in actual field environments, including soils. The mechanism can only operate when the particles are free to move in order to align themselves, as in aqueous solutions, and could also potentially occur when nanoparticles nucleate next to each other on a solid substrate, through heterogeneous nucleation.

3.2.9 Nanoparticle Sorption, Redox Phenomena, and Catalysis

Because the basic properties of materials may be different at the nanoscale than at the bulk scale, and given the high surface areas of nanoparticles, an important question concerns the controls on sorption to nanoparticles and whether nanoparticles sorb ions and molecules differently than do larger, bulk materials. There are many different concepts and properties that must be considered in studies of these phenomena.

First, a few comments on “sorption” terminology are needed. The term “sorption” is used when the mechanism by which an adsorbate accumulates in association with a solid the adsorbent is unknown, or to refer to more than one process. Adsorption is the term of choice for a process in which individual species or small clusters accumulate in a two-dimensional fashion at an external surface. Absorption refers to accumulation that goes into a particle, such as into clay interlayers or micro pores. Precipitation refers to a three-dimensional accumulation process associated with a surface, known as heterogeneous nucleation, or in the surrounding solution, known as homogeneous nucleation. Sorption phenomena often may play a role in redox reactions and catalysis (Huang, 1999).

Sorption is generally quantified in terms of moles (or grams) of sorbate per meter squared of sorbent surface area, with specific surface area generally measured by gas adsorption (or desorption) using the BET method (Brunauer et al., 1938). However, nanoparticles often aggregate during BET measurements, which can make it difficult to measure specific surface area reliably. Some nanomaterials may recrystallize, dehydrate, or otherwise change in shape and/or structure as a result of the temperature changes that occur during BET sample preparation and measurements, and this process needs to be considered in developing measurement protocols (Maurice et al., 2000).

Other techniques commonly used to characterize particles for use in sorption experiments also require special care when applied to nanoparticles. For example, measurements of electrophoretic mobility, or zeta potential, are often used to determine particle point of zero charge. Most commercial instruments apply the Smoluchowski equation for electrophoretic mobility, but this equation tends to break down for very small particles, and other approaches need to be considered (O’Brien and White, 1978; Maurice, 2009). Particle shape and suspension density can also be important, especially for nanoparticles, and particle aggregation is important because it can affect mobility.

Because the surface properties of nanoparticles change with particle size, we can expect sorption phenomena to be sensitive to particle size, as well. For example, titration experiments showed that the point of zero charge (pHzc) of titania...
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nanoparticles changes with nanocrystalline size (Finnegan et al., 2007); differences in point of zero charge affect surface potential and can influence sorption behavior as a function of pH. Ha et al. (2009a, 2009b) investigated Zn(II) adsorption to hematite micron- versus nanoscale nanoparticles. They observed differences in adsorption complex structure and in formation of Zn-containing precipitates with hematite particle size.

Many particles in nature may have nanoscale porosity that can be very important for fate and transport of metals, radionuclides, and organic compounds. For example, the d-spacings of swelling clays such as montmorillonite, may swell to the nanometer scale, with thickness of the interlayer region itself approaching 1 nm. Sposito et al. (1999) showed that the structure of water in montmorillonite interlayers appears to be different from the structure of bulk water in solution. Hydrophobic organic compounds and organic cations may absorb in clay interlayers (Lagaly, 1981; Boyd et al., 2001; He et al., 2006) and the conformations of the absorbed organic molecules may be different from their conformations in bulk solution (Haack et al., 2008). Absorption into interlayers and nanoparticles can be important to contaminant fate and transport, and more research needs to be focused on the hydrology, hydraulics, structure of water, and reactivity of water and solutes in nanoscale spaces.

Because of growing concerns over greenhouse gas emissions and climate change, recent study is focusing on nanoscale sorption phenomena for CO2 capture. A current method for scrubbing CO2 from power-plant emissions is the use of liquid amine as a solution absorbent. However, reversible capture by sorption on a solid phase could offer significant benefits. CO2 may diffuse into the clay mineral pyrophyllite (Wang and Zhang, 2003) and sericite (fine-grained muscovite; Zhang et al., 2005) during dehydroxylation, but the potential extent of uptake and reversibility are not known. Fibrous clays such as palygorskite have channels that can take up water and SO2 (Zhang et al., 2009); CO2 uptake seems likely but is yet to be fully explored (R. Cygan, Sandia National Lab, personal communication, 2010). Zeolites and carbon molecular sieves can reversibly sorb significant quantities of CO2 at room temperature, but they are less efficient at higher temperatures and have poor selectivity with respect to water (Zheng et al., 2005). Considering the success in using liquid amine for CO2 capture, research is focusing on amine-modified (nano)porous materials such as silica gels and polymers and mesoporous silica (Zheng et al., 2005).

For nanoparticles, size quantization of the electron structure, coupled with changes to surface structure and surface defect site density, may lead to different rates of electron transfer in redox reactions. Madden and Hochella (2005) showed that the rate of heterogeneous manganese oxidation by hematite nanoparticles is up to one and a half orders of magnitude greater for 7.3 nm average diameter particles than for 37 nm particles. This effect was apparent even when surface area was taken into consideration in the rate calculations.

Nanoparticles may have particularly useful catalytic properties because of the high surface areas they expose to the atmosphere or to solution and because of differences in surface structure, electron transfer properties, and other characteristics. For example, TiO2 nanoparticles are widely used in photocatalysis applications (Aitken et al., 2006), and they have been shown to photocatalyze the degradation of pollutant organics (Armaleo et al., 2007). The heterogeneous Mn oxidation by hematite nanoparticles observed by Madden and Hochella (2005) is an example of a natural catalytic process. Nevertheless, although catalysis by nanoparticles is a topic of significant industrial research, far less is known about the potential catalytic properties of nanoparticles in nature.

3.3 Nanoparticle Mobility in Soils and Sediments

The small size of nanoparticles has important implications for their mobilities in porous media. According to Stokes’ Law, particle settling velocity ($v_s$) (m s$^{-1}$) increases with the particle size ($d_p$) (m) and density ($\rho_p$) (kg m$^{-3}$):

$$v_s = \frac{g(\rho_w - \rho_p)d_p^2}{18\mu}$$  \hspace{1cm} (3.10)

where

- $g$ is the acceleration due to gravity (9.807 m s$^{-2}$)
- $\rho_w$ is the density of water (kg m$^{-3}$)
- $\rho_p$ is the particle density (kg m$^{-3}$)
- $\mu$ is the absolute viscosity of the water (Pa s or kg m$^{-1}$ s$^{-1}$)

Thus, when we consider nanoparticle mobility in porous media, it needs to be recognized that individual nanoparticles are subject to translational diffusion and Brownian motion, but that they are too small to be strongly affected by gravity.

DLVO theory, named after work by Derjaguin and Landau (1941) and Verwey and Overbeek (1948), has been widely used to help predict colloid stability as well as the sorption of colloids to sediment (i.e., collector) surfaces in porous media. In classical DLVO theory, the stability of particles in suspension is dependent upon total potential energy $V_T$:

$$V_T = V_A + V_R + V_S$$  \hspace{1cm} (3.11)

which is the sum of

- $V_A$, potential energy due to attractive van der Waals forces
- $V_R$, potential energy due to repulsive, electrical double layer, forces
- $V_S$, potential energy due to the solvent, which is generally small and often neglected in the calculations

This classical DLVO theory has been expanded recently to include other forces of interaction such as Born repulsion and Lewis acid–base interaction (Grasso et al., 2002; Saiers and Ryan, 2005).

One of the challenges in dealing with nanoparticle aggregation and adsorption to surfaces of porous media is that classical and extended DLVO theories were developed for particles whose
radius of curvature is greater than the thickness of the double layer, and this is often not the case for nanoparticles. Many interfacial forces, such as electrostatic and van der Waals, can extend over distances that are large in comparison with the size of an individual nanoparticle. Surface and interfacial forces that are not considered in classical DLVO theory, such as hydration/solvation and Born repulsion, are likely to be particularly important for interactions between nanoparticles or between a nanoparticle and a sediment particle (collector) surface (Maurice, 2009).

A great deal of recent research is focused on nanoparticle aggregation and how it affects mobility in porous media. Indeed, the two are linked because aggregated particles have been shown to transport differently than individual (colloidal) particles (Waite et al., 1991). Recently, Gilbert et al. (2007) investigated controls on aggregation of (highly disordered) goethite nanoparticles. Based on extensions to DLVO theory, particles of like charge should be unlikely to form stable aggregates because of repulsion between the like charges. However, aggregation can occur in solutions that have enough thermal energy to overcome this barrier to aggregation. Gilbert et al. (2007) observed the formation of nanoparticle aggregates or nanoclusters between pH 5 and 6.6, with diameters from 25 to ~1000 nm, which remained stable in suspension for at least 10 weeks. This formation of stable nanoclusters of an Fe(III)(hydr)oxide indicates that more attention needs to be paid to the role of nanoclusters in transport in porous media, especially given that many pollutants tend to adsorb to Fe(III)(hydr)oxide minerals.

A good deal of research is also focused on the suspension and aggregation of fullerenes in aqueous solutions. The fullerene C_{60} tends to be highly insoluble in water, but may be induced to form aqueous suspensions by prolonged stirring (Brant et al., 2005). Ma and Bouchard (2009) showed that suspended C_{60} nanoclusters form upon prolonged stirring can remain as stable aggregates in suspension for weeks or longer. The nanoclusters of C_{60} tend to exhibit pH-dependent surface charge, as measured by zeta potential. The mechanism whereby the surface charge is developed on the C_{60} nanoclusters in suspension is not yet understood (Ma and Bouchard, 2009). In any case, there is much that we presently do not know about fullerene surface properties, charge, aggregation behavior, and potential transport through porous media, particularly under hydrologically unsaturated conditions and in long-term environmental exposure.

In hydrologically saturated porous media, it has been shown that colloids may be removed from the solution phase by sorption to the collector surfaces and/or pore straining, which is the trapping of particles in small pores. Many groups are investigating nanoparticle mobility in saturated porous media. Wang et al. (2008) investigated the retention and mobility of C_{60} aggregates in saturated columns packed with Ottawa sand and or glass beads. Retention of the aggregates was considerably greater in the presence of 1.0 mM CaCl$_2$ versus in deionized water without added electrolyte, due at least in part to electrostatic interactions.

In unsaturated conditions, as commonly encountered in soils, colloidal particles may be trapped by a thin film of water on collector surfaces, in a process known as film straining (Chen et al., 2008 and references therein). Colloids may also adhere to the air–water interface, and colloids can be found associated with bubble walls (Wan et al., 1994). Chen et al. (2008) observed that TiO$_2$ nanoparticle mobility was affected by the saturated/unsaturated ratio in porous media and suggested that the nanoparticles may adsorb to the air–water interface.

Particle aggregation has been shown to play an important role in colloid mobility in porous media, and its effects on nanoparticle mobility are also being explored. Guzman et al. (2006) investigated the effects of pH on TiO$_2$ nanoparticle aggregation and transport in hydrologically saturated porous media consisting of two-dimensional microfluidic devices. They found that transport was influenced by both surface potential effects and size of nanoparticle aggregates. Nanoparticle aggregates could become clogged in pores (Figure 3.9). An important question raised was whether nanoparticle aggregates would behave similarly to colloidal particles and aggregates of colloids. For example, nanoparticle aggregates might potentially break apart or otherwise be altered by the presence of shear in flowing porous media.

Questions of natural and manufactured nanoparticle aggregation and transport in porous media are reviving interest in humic substances research. Humic substances are well known to affect colloid aggregation, fate, and transport, and are likely to

![Figure 3.9](image_url)
be equally or even more important for nanoparticles. Chen and Elimelech (2008) investigated $C_{60}$ deposition kinetics onto bare silica surfaces or surfaces precoated with natural organic matter (NOM) in the form of humic acid (Figure 3.10) or alginate. They observed that preadsorbed NOM on the silica surface can either retard or enhance the deposition kinetics, depending on the solution ionic composition and the physicochemical properties of the NOM. On the other hand, the presence of NOM in solution tended to decrease deposition, which the authors attributed to steric repulsion upon NOM sorption. This suggests that the effects of NOM, including humic substances, can be complex and different in diverse environments such as soils, groundwaters, or colloid-containing surface waters.

### 3.4 Nanotoxicity

Many engineered nanoparticles have the potential to be toxic to humans and/or ecosystem components such as microorganisms, plants, aquatic, and other organisms (NRC, 2008; Wiesner et al., 2008). A recent report from the National Research Council (NRC, 2008) stressed the pressing need for a national strategy for nanorisk research to evaluate the environmental health risks of nanotechnologies and engineered nanoparticles. The field of nanotoxicology is one of the new disciplines that has emerged over the last decade as an outgrowth of the explosion of research and development in nanoscience and nanotechnology. As pointed out by Oberdorster et al. (2005), the small size of nanoparticles makes it much easier for them to penetrate pores in skin, to be integrated into the respiratory system, and to penetrate cells. The high surface areas of nanoparticles can make them far more bioreactive. Thus, there is much real concern about nanotoxicity, especially given that so many new engineered nanoparticles are being released to the environment without toxicology analysis.

In some instances, the toxicity of nanoparticles is being touted for its potential health benefits, for example, as microbicide agents. Sondi and Salopek-Sondi (2004) showed that Ag nanoparticles have strong antimicrobial effects against *Escherichia coli*. Electron microscopy revealed clear cell damage, including pits in the cell walls and Ag nanoparticle accumulation in the microbial membrane (Figure 3.11). Results such as these are leading to widespread use of Ag nanoparticles as antimicrobial agents in detergents, on clothing, and in other applications.

![FIGURE 3.10](image1.png)

**FIGURE 3.10** The attachment efficiencies of $C_{60}$ nanoparticles on silica with and without humic coating in (a) NaCl and (b) CaCl₂. (With permission from Chen, K.L., and M. Elimelech. 2008. Interaction of fullerene ($C_{60}$) nanoparticles with humic acid and alginate coated silica surfaces: Measurements, mechanisms, and environmental implications. Environ. Sci. Technol. 42:7607–7614. Copyright 2008 American Chemical Society.)

![FIGURE 3.11](image2.png)

**FIGURE 3.11** Silver (Ag) nanoparticles have toxic effects on *E. coli*. A TEM image of *E. coli* following exposure to Ag nanoparticles for 1h. (With permission from Sondi, I., and B. Salopek-Sondi. 2004. Silver nanoparticles as antimicrobial agent: A case study on *E. coli* as a model for Gram-negative bacteria. J. Colloid Interface Sci. 275:177–182. Copyright 2004 American Chemical Society.) Some particles have penetrated into the cell. Intracellular materials have leaked into the medium surrounding the cell and Ag nanoparticles are attached to this material. This nanoparticle toxicity is leading to the use of Ag nanoparticles as antimicrobial agents in many products from detergents to dissemination on clothing.
Nanotoxicity to plants, or nanophytotoxicity, is another area of growing research. Lin and Xing (2008) found that ZnO nanoparticles had a (phyto)toxic effect on Ryegrass (*Lolium perenne*). The ZnO particles adsorbed into root tissues and cells and damaged the root tissues, inhibiting seedling growth. The phytotoxicity could not be explained by dissolution of ZnO particles, and dissolved Zn, but rather appeared to result from the actual nanoparticles themselves.

### 3.5 Nanoenabled Sensing

The revolution in nanotechnology promises to have another major impact on soil science in the form of nanoenabled sensing. There are many nanodevices that can be used for in situ sensing of soil components. Lee et al. (2008) developed colorimetric uranium sensors based on a uranyl (UO$_2$$^{2+}$)-specific DNAzyme and gold nanoparticles (AuNP). A DNAzyme is essentially a DNA molecule that changes its fluorescence properties upon sorption of a specific component such as uranyl. In the nanosensor approach, uranyl-specific DNAzyme was attached to AuNP, forming functionalized purple aggregates. Uranyl-induced disassembly of the functionalized AuNP aggregates, resulting in individual AuNPs that were red in color. This nanosensor system was shown to have a detection limit of 50 nM uranyl.

Many other groups are using nanotechnology to develop sensors, or sensors that are approaching the nanoscale, specifically for soil applications. Bendikov et al. (2005) developed flexible, miniature, and inexpensive nitrate sensors that are fabricated by electropolymerizing pyrrole onto carbon fiber substrates using nitrate as a dopant. The resulting sensor shown in Figure 3.12 (length 1 cm or less, micron-scale diameter) is ideal for deployment in the pore space of soils and sediments and can quantify nitrate concentrations to just below 10$^{-4}$ M. Although this sensor is not nanoscale per se, it demonstrates the trend in miniaturization that is occurring in environmental sensors for soil applications.

### 3.6 Frontiers in Research in Nanoscale Particles and Processes in Soil Environments

Soil science is very much at the center of nanoscience and nanotechnology. On the one hand, soils are replete with natural nanoparticles and soil scientists have a long and distinguished history of investigating small particles in nature. On the other hand, nanoengineering is resulting in the release of an enormous number and diversity of nanoparticles to the environment, and they are certain to find their way into soils. Nanotechnology also is contributing to a new generation of sensors that can be used to investigate a host of soil parameters and processes.

Some frontiers for research involving soil science and the nanoscale include the following:

1. **What are the unique properties of water in nanopores?**
2. **What are the controls on nanoparticle aggregation kinetics, and how do soil components such as NOM, mono- and multi-valent ions, and bacteria affect aggregation of natural and engineered nanoparticles?**
3. **What are the controls on nanoparticle mobility not only in the saturated zone but also in hydrologically unsaturated environments?**
4. **What are the fundamental controls on nanotoxicity, and how can we prevent potentially toxic engineered nanoparticles from entering the food supply?**
5. **How well does our new primarily laboratory-based understanding of nanoparticles and nanoprocesses translate to real-world environments, including soils?**
6. **What implications will our ability to detect and study nanoparticles in soils and water have for various nations’ regulatory structures related to pollutants?**
7. **How can nanotechnology best be used in soil science and broader agricultural applications, from sensing to treatment of crop diseases to controls on soil porosity, structure, and fertility?**
8. **How can we best harvest the strengths of nanoscience and nanotechnology while at the same time minimizing the risks to environmental and human health?**
9. **How can the unique abilities and perspectives of soil scientists be harnessed to contribute most successfully to the broader nanoscience and nanotechnology communities?**

Given the unique properties and behaviors of nanoparticles, and the burgeoning of nano research and development, it is impossible to predict the potential long-term costs and benefits to soils and agriculture. One certain fact is that the soil community, with its long history of dealing with complex systems of small particles, has a great deal to contribute to understanding complex environmental processes at the nanoscale.
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