Unique forms of manufactured nanomaterials, nanoparticles, and their suspensions are rapidly being created by manipulating properties such as shape, size, structure, and chemical composition and through incorporation of surface coatings. Although these properties make nanomaterial development interesting for new applications, they also challenge the ability of colloid science to understand nanoparticle aggregation in the environment and the subsequent effects on nanomaterial transport and reactivity. This review briefly covers aggregation theory focusing on Derjaguin-Landau-Verwey-Overbeak (DLVO)-based models most commonly used to describe the thermodynamic interactions between two particles in a suspension. A discussion of the challenges to DLVO posed by the properties of nanomaterials follows, along with examples from the literature. Examples from the literature highlighting the importance of aggregation effects on transport and reactivity and risk of nanoparticles in the environment are discussed.

As of the submission date of this review, approximately 4700 articles on nanoparticle (NP)-related topics have been published in the calendar year 2009 alone (Thompson Reuters, 2009). Many of these papers discuss novel particles, and applications of nanomaterials along with their use in consumer products are expanding rapidly (Project on Emerging Nanotechnologies, 2009). For example, nanomaterials are used for environmental clean-up and biomedical applications (Alivisatos, 2001; Liu et al., 2005). This expansion in applications, and the incorporation of “nano” ingredients into products that may be released during the life cycle of those products, will increase the occurrence of manufactured nanomaterials in the environment. For example, the leaching of silver NPs used as antimicrobial agents in cloth was recently reported (Benn and Westerhoff, 2008). Unintentionally or intentionally, manufactured NPs might come into contact with biological receptors. For this reason, the risk of nanomaterials to humans and to the environment garners attention from the scientific community, governmental agencies, and public stakeholders.

Nanoparticles in engineered or environmental systems could be thought of as dispersions of primary particles. However, primary NPs tend to aggregate into clusters up to several microns in size (Brant et al., 2007; Chen and Elimelech, 2007; Jiang et al., 2009; Limbach et al., 2005; Phenrat et al., 2008). Therefore, NP aggregation plays an important role in determining reactivity, toxicity, fate, transport, and risk in the environment. The critical role of aggregation in environmental implications had occasionally been ignored (Baveye and Laba, 2008), but many recent studies have begun applying colloid science principles, based around Derjaguin-Landau-Verwey-Overbeak (DLVO) theory, to understand NP aggregation under various conditions. Manufactured NPs challenge the limits of colloid science, however, due to their small size, variable shape, structure, composition, and potential presence of adsorbed or grafted organic macromolecules. Laboratory aggregation studies, which are covered in detail in this review, have demonstrated that these challenges, acting simultaneously, will ultimately affect how NPs behave in the environment. Additionally, particles released to the environment undergo...
chemical and physical transformations and encounter a multi-
tude of solution conditions important for aggregation, includ-
ing solution pH, dissolved ions, naturally occurring organic
matter, clays, and biocolloids.

This review focuses on three questions: (i) Can basic colloid
science predict the behavior of nanomaterials in the environ-
ment? We provide a brief overview of colloid science. Several
excellent resources are available for additional information
on colloid science (Evans and Wennerstrom, 1999; Hiemenz
and Rajagopalan, 1997; Buffle et al., 1998; Elimelech and
O’Melia, 1990; O’Melia, 1980). (ii) Where are challenges to
existing theory posed by manufactured nanomaterials? We
discuss the intrinsic NP properties that raise these challenges.
(iii) How will these challenges affect studies of fate and trans-
port, reactivity, and risk to the environment? We describe
several case studies examining environmental implications
of nanomaterial aggregation.

Colloid Science and Aggregation
Colloid science is defined as a branch of chemistry dealing with
colloids, heterogeneous systems consisting of a mechanical
mixture of dispersion (colloids) and dispersant. When particles
are dispersed, sizes range between 1 nm and 1 μm in a continu-
ous medium. Above this size range, particles begin to sediment
out of suspension. Several theories to explain aggregation of
submicrometer spherical particles have been developed and
experimentally studied for decades, the most common being
dLVO (Derjaguin and Landau, 1941; Verwey et al., 1948)
an alternative approach is statistical thermodynamics; see
Hermansson [1999] and Koponen [2009]). By definition, the
size range of colloidal particles overlaps the size range of manu-
factured nanomaterials (i.e., <100 nm). Therefore, theories in
colloid science should be applicable to manufactured nano-
materials, but, due to the novelty of nanomaterial properties, sev-
eral studies have found that this is not always the case (He et
al., 2008; Kozan et al., 2008; Phenrat et al., 2008). However,
colloid science is fundamental to understanding and develop-
ing theories for nanomaterials systems. This section, therefore,
provides a very brief review of the types of aggregation and
dLVO theory.

Types of Aggregation and Aggregate Structure
Aggregation of colloidal particles occurs when physical pro-
cesses bring particle surfaces in contact with each other and
short-range thermodynamic interactions allow for particle–
particle attachment to occur. For particles <100 nm in size,
Brownian diffusion controls the long-range forces between
individual nanoparticles, causing collisions between particles.
When contact occurs, it can result in attachment or repul-
sion. Short-range thermodynamic interactions that control
this can be understood in the context of dLVO theory. There
are two types of aggregation relevant to manufactured NPs in
the environment: homoaggregation and heteroaggregation.
Homoaggregation refers to aggregation of two similar par-
ticles (i.e., NP–NP attachment). This is observed in homo-
genous suspensions of particles that are typically studied in
the laboratory to make useful correlations with dLVO theory.
Heteroaggregation refers to aggregation of dissimilar particles
(e.g., NP–clay particle attachment). Real environmental sys-
tems contain natural particles (e.g., clay particles) in numbers
far greater than the number of manufactured NPs, so heteroag-
gregation is an important fate process for manufactured NPs.

The probability that two particles attach is given by a “stick-
ing coefficient,” also known as the attachment efficiency (α)
(i.e., when α = 1, sticking occurs 100% of the time; when α =
0.5, sticking occurs 50% of the time). Particles attaching at first
contact (α = 1) form large dendritic aggregates, whereas par-
ticles sticking only after several collisions (α < 1) form denser
and less dendritic aggregates (Buffle and Leppard, 1995). The
concept of fractal dimension is used to describe aggregate struc-
ture. Fractal dimension (Df) can range from 1 (a line) to 3 (a
sphere). These are limits that come from Euclidean dimension,
where 1 is a straight line (e.g., x1), 2 is a flat surface (e.g., x2),
and 3 is a volume (e.g., x3). Fractal dimensions are those that
lie between Euclidean dimensions. Ideal fractal structures are
self-similar throughout. Homoaggregation under controlled
laboratory conditions produces aggregates of reasonably pre-
dictable fractal dimension (Barbot et al., 2010; Chakraborti
et al., 2003; Hansen et al., 1999), whereas heteroaggregation
typically forms natural fractals (statistically self-similar over a
limited range of length scales), making aggregation state more
difficult to predict. The physical dimensions of the aggregates
formed can affect the reactive surface area, reactivity, bioavail-
ability, and toxicity. Aggregate structure must therefore be
determined and considered when interpreting fate, transport,
and toxicity data.

Derjaguin-Landau-Verwey-Overbeak and Extended
Derjaguin-Landau-Verwey-Overbeak
According to the classical dLVO theory of aggregation, the
sum of attractive and repulsive forces determines attachment
(Derjaguin and Landau, 1941; Verwey et al., 1948). This
theory maintains that only two forces dominate interactions
between particles: van der Waals (vdW) attractive and electro-
static double layer (EDL) forces. Table 1 lists an expression for
the vdW attraction experienced by two spheres in suspension
(Stumm and Morgan, 1996). Expressions for vdW commonly
calculate the attraction between two spherical particles; how-
ever, due to unique NP shapes and compositions, expanded
theoretical approaches may be needed (Gatica et al., 2005).
An EDL has a charge that reflects not only the surface that it
surrounds but also the solution chemistry of the surrounding
media. Ionic strength, which is a measure of the amount of
ions present, controls the extent of the radius of the diffuse
layer from the surface. Low ionic strength means the EDL ion
cloud extends far out from the particle; high ionic strength
conditions compress the EDL. Table 1 lists an expression for
the EDL experienced by two charged spheres in suspension
(Stumm and Morgan, 1996). Classical dLVO simplifies thermodynamic surface inter-
actions and predicts the probability of two particles stick-
ing together by simply summing van der Waals and electric
double-layer potentials to determine if forces are net attractive
(−VT) or net repulsive (+VT). For example, in Fig. 1, van der
Waals and electric double-layer potentials are plotted as a func-
tion of separation distance between the particles. Summing
these curves \( (V_T) \) demonstrates that particles can have a net attraction in a primary or secondary minimum (well). Particles in the primary well are considered to be irreversibly aggregated, whereas particles in the secondary well are reversibly aggregated (i.e., re-entrainment is possible if shear forces are exerted) (Hahn et al., 2004). Figure 1 also shows something

<table>
<thead>
<tr>
<th>Force</th>
<th>X/DLVO†</th>
<th>Equations‡§</th>
<th>Origin</th>
<th>References</th>
</tr>
</thead>
</table>
| van der Waals attraction | DLVO    | \[
\frac{V_{\text{VDW}}}{kT} = -\frac{A}{6\kappa T} \left( \frac{2a^2}{(4a + s)^2} \right) + \frac{2a^2}{(2a + s)^2} \ln \left( \frac{4a + s}{2a + s} \right)
\] | interactions of electrons in particles | Stumm and Morgan (1996) |
| Electrostatic double layer | DLVO    | \[
\frac{V_{\text{EDLVO}}}{kT} = \frac{4\pi n k T}{\kappa} \left( \frac{\delta + \delta}{s + 2a} \right) \left[ \text{tanh} \left( \frac{\Psi_d}{4kT} \right) \right]^2 \exp \left( -\kappa \right)
\] | charged surfaces | Delgado et al. (2007), Stumm and Morgan (1996) |
| Magnetic attraction    | XDLVO   | \[
V_M = -\frac{8\pi \mu M_s^2 a^3}{9\left( s + 2a \right)}
\] | aligning electron spins | Phenrat et al. (2007) |
| Hydrophobic (Lewis acid-base) | XDLVO | \[
\frac{V_{\text{AB}}}{\text{surface area}} = \Delta G^{\text{AB}} \exp \left( \frac{s_0 - s}{\lambda} \right)
\] | entropic penalty of separating hydrogen bonds in water | Hoek and Agarwal (2006), Wu et al. (1999) |
| Osmotic repulsion      | XDLVO   | \[
2d \leq s \Rightarrow \frac{V_{\text{OSM}}}{kT} = 0
\] | concentration of ions between two particles (Fig. 4) | Fritz et al. (2002), Ortega-Vinuesa et al. (1996), Phenrat et al. (2008), Romero-Cano et al. (2001) |
| Elastic-steric repulsion | XDLVO | \[
\text{d} \leq s < 2d \Rightarrow \frac{V_{\text{dim}}}{kT} = \frac{a^2\pi}{n_1} \left[ \left( \frac{1}{2} - \chi \right) d^2 - \left( \frac{1}{2} - \ln \left( \frac{d}{s} \right) \right) \right]
\] | molecules on particle surfaces resist loss of entropy due to compaction | Fritz et al. (2002; Ortega-Vinuesa et al., 1996; Phenrat et al., 2008; Romero-Cano et al., 2001) |
| Bridging attraction    | XDLVO   | NA          | surface molecules bridge to other particles | Chen and Elimelech (2007), Domingos et al. (2009) |

† DLVO, Derjaguin-Landau-Verwey-Overbeek; EDLVO, extended Derjaguin-Landau-Verwey-Overbeek.

‡ A, Hamaker Constant; a, average particle radius; \( \chi \), Flory-Huggins solvency parameter; d, thickness of “brush” polymer layer (\( \sim \)); \( \Delta G^{\text{AB}} \), free energy of acid base interaction between particles at distance \( s \); \( \delta \), Stern layer thickness; \( \varepsilon \), relative permittivity of water (\( =78.5 \text{ C V}^{-1} \text{ m}^{-1} \)); \( \varepsilon_0 \), permittivity of a vacuum (\( =8.854 \times 10^{-12} \)); e, elementary charge of an electron; \( \kappa \), inverse Debye length; \( k \), Boltzmann constant; \( \lambda \), decay length for acid–base interactions (\( \approx 0.6 \text{ nm} \)); \( M_s \), saturation magnetization; \( \mu_0 \), vacuum permeability; \( n \), number concentration of ion pairs; \( \rho_p \), density of polymer; \( \Psi_d \), diffuse potential (\( \sim \)zeta potential); s, distance between interacting surfaces; \( s_0 \), minimum equilibrium separation distance (\( \approx 0.158 \text{ nm} \)); T, absolute temperature; \( \phi_p \), volume fraction of polymer in “brush”; \( \nu_v \), volume of solvent molecule; z, electrolyte valence.

§ Refer to referenced publications for details of equation derivations and constraints.
that is commonly the case with manufactured NPs having an organic coating: Classical DLVO forces alone are not sufficient to accurately predict aggregation behavior. Steric repulsion forces ($V_T + V_{ELAS}$) resulting from adsorbed polymer or poly-electrolyte coatings or natural organic matter (NOM) makes it so these particles may only have a net attraction in a secondary minimum. Coated NPs may therefore aggregate reversibly (Graf et al., 2009), and aggregation reversibility has significant consequences regarding the fate, transport, bioavailability, and effects of NPs in the environment. These additional forces are collectively known as extended DLVO (XDLVO).

In addition to steric repulsion forces ($V_T + V_{ELAS}$) due to NP coatings, other XDLVO forces have been invoked to match experimental data for various types of aggregating primary particles (Chen and Elimelech, 2007; Fritz et al., 2002; Hoek and Agarwal, 2006; Ortega-Vinuesa et al., 1996; Phenrat et al., 2007; Phenrat et al., 2008; Romero-Cano et al., 2001; Wu et al., 1999). This means that additional short-range forces are operating on an equivalent magnitude as vdW attraction and EDL. These forces can include bridging (Chen and Elimelech, 2007), osmotic (Fritz et al., 2002; Ortega-Vinuesa et al., 1996; Phenrat et al., 2008; Romero-Cano et al., 2001), steric (Fritz et al., 2002; Ortega-Vinuesa et al., 1996; Phenrat et al., 2008; Romero-Cano et al., 2001), hydrophobic Lewis acid-base (Wu et al., 1999) (Hoek and Agarwal, 2006), and magnetic forces (Phenrat et al., 2007). Table 1 summarizes these forces. The relevant force type depends on the system tested, and frequently more than one XDLVO force is important. Moreover, forces are not completely independent of one another. In the case of nanomaterials, understanding aggregation using a DLVO- or XDLVO-based theory presents many challenges.

**Nanoparticle Challenges to Derjaguin-Landau-Verwey-Overbeak**

Colloid science demonstrates that several forces with different natures and origins govern the kinetics and extent of particle aggregation. This section elaborates how manufactured NPs present a combination of challenges to two predominant theories in colloid science, DLVO and XDLVO. Among these challenges are shape, size, structure, composition, and adsorbed or grafted organic macromolecules (e.g., coatings or NOM) (Fig. 2). Although particles not classified as “nano” (i.e., <100 nm) also present some of these challenges, manufactured NPs are often designed with the intention of amplifying these properties. Examining some early studies demonstrating these challenges can inform our discussion in the previous section on implications of NP aggregation on their transport and reactivity in the environment.

**Particle Size**

The small size of most NPs conflicts with a fundamental assumption of DLVO. Equations describing EDL are mathematically incorrect if this assumption does not hold (Delgado et al., 2007). This is because when a particle reaches a small enough size, its surface curvature is too substantial to assume it is flat (i.e., when the assumption of $\kappa \cdot a >> 1$ no longer applies). Therefore, this is one of the primary challenges when considering NP aggregation in a DLVO framework. Aside from this, vdW and EDL forces (Table 1) scale similarly with particle size (Evans and Wennerstrom, 1999; Hiemenz and Rajagopalan, 1997; Israelachvili, 1991), so moving from microscale to nanoscale particles should theoretically affect a change on vdW and EDL forces to a similar degree. However, as a particle decreases in size, a greater percentage of its atoms exist on the surface. Electronic structure, surface charge behavior, and surface reactivity can be altered as a result. Recent studies suggest that redistribution and changing coordination environment of charge and atoms at the surfaces of NPs strongly influences their reactivity (Hochella et al., 2008). He et al. (2008) reported that as the particle size became smaller, the particles became more susceptible to surface charge titration. They found an inverse correlation between particle size and the measured point of zero charge (PZC); 12, 32, and 65 nm hematite particles had PZCs of 7.8, 8.2, and 8.8 pH units, respectively (He et al., 2008). These hematite NPs were synthesized using the same method so they would be identical in every aspect except for size. However, for these particles, at pH 7 the smaller particles are less charged than larger particles, leading to lower EDL repulsion forces and subsequently greater aggregation tendency. Indeed—given the same ionic strength—smaller hematites have faster aggregation rates than larger ones (He et al., 2008). This suggests that size polydispersity in manufactured NPs affects their aggregation behavior.

Polydispersion is the reality in large-scale applications. For example, reactive nano-scale zerovalent iron (NZVI) particles used for environmental remediation are highly polydisperse (Liu et al., 2005; Phenrat et al., 2007; Phenrat et al., 2009a). Unlike van der Waals attraction, long-range magnetic attraction between two NZVI particles increases with particle radius to the sixth power (Table 1). Polydispersity and particle size therefore greatly affected the aggregation of NZVI having particle sizes ranging from 15 to 260 nm, with aggregation being proportional to the fraction of large particles in the dispersion (Phenrat et al., 2009a).

Fig. 1. van der Waals force (dashed line), electrostatic double layer (EDL) force (gray line), total Derjaguin-Landau-Verwey-Overbeak (DLVO) forces, and elastic force plotted together to find total potential as a function of separation distance. XDLVO, extended Derjaguin-Landau-Verwey-Overbeak. V/KT, potential energy divided by Boltzmann’s constant and absolute temperature.
Another example of a size effect is “halo” stabilization, where nano-sized materials can control electrostatic repulsion between two approaching micrometer-sized particles, hindering their flocculation by keeping them separated beyond the range of DLVO attractive forces (Fig. 3). Tohver et al. (2001) found that adding 6-nm zirconia NPs to a dispersion of unstable submicron silica particles (0.6 μm in diameter) stabilized the mixture (Tohver et al., 2001). The same phenomenon was observed for bimodal magnetorheological fluids consisting of micrometer sized magnetite particles (1.45 μm in diameter) and magnetite NPs (8 nm diameter) (Viota et al., 2007). Size and resultant polydispersity, therefore, present a large challenge to understanding how NP dispersions behave because these parameters can enhance or diminish aggregation.

**Chemical Composition**

Colloid science captures the effect of chemical composition on aggregation through the Hamaker constant, which governs van der Waals attraction; saturation magnetization, which controls magnetic attraction; hydrophobicity, which controls hydrophobic interaction (Wu et al., 1999); and surface charge, which governs electrostatic double layer (EDL) interaction (Table 1) (Evans and Wennerstrom, 1999).

Particles with a high Hamaker constant have greater aggregation tendency compared with particles with a low Hamaker constant at the same solution and surface chemistry. Because the origin of van der Waals attraction is permanent or induced dipoles, a bulk material with electronic or molecular structure that favors generation of permanent or induced dipoles normally has a large Hamaker constant value. For example, the Hamaker constants of gold, silver, and polystyrene are 45.3, 39.8, and approximately $9.8 \times 10^{-20}$ J, respectively (Hiemenz and Rajagopalan, 1997). van der Waals attraction forces are approximately five times stronger for gold particles in comparison with polystyrene (see equation in Table 1). In addition to controlling van der Waals attraction, some materials can originate forces that challenge the DLVO framework, including magnetic and hydrophobic interactions that promote aggregation. For example, ferromagnetic and ferrimagnetic materials, such as zerovalent iron and magnetite, can cause long-range magnetic attraction without an applied magnetic field (Table 1) (Elena et al., 2009; Phenrat et al., 2007). This magnetic force contributes to abnormally rapid aggregation. Moreover, carbon-based nanomaterials, such as C₆₀ or CNTs, have hydrophobic surfaces in aqueous environments. Interaction of all-carbon surfaces with water molecules involves a significant entropic penalty driving an aggregation process that might
be understood through the use of XDLVO frameworks that model hydrophobic Lewis acid–base interactions (Wu et al., 1999). These types of XDLVO frameworks have yet to be developed for carbon-based nanomaterials.

Unique NP composition and morphology (e.g., core-shell NPs) and environmental transformations of NPs will challenge DLVO explanations of aggregation. Particles with a high surface potential have lower aggregation tendencies compared with particles with a low surface potential given the same solution chemistry. Nanoparticle chemical composition alters surface potential by dissociation or ion adsorption by surface atoms (Evans and Wennerstrom, 1999; Israelachvili, 1991). Surface charge of uncoated NPs is therefore governed in part by the type of atoms at the surface of the particles. However, the core of core-shell particles, which are common, can influence the charge of the surface atoms. For example, uncoated FeO/Fe3O4 core-shell NPs have a zeta potential near −32 mV (in 1 mmol L−1 NaHCO3 at pH 7.5), but as the FeO core of the particles oxidizes to magnetite, the surface charge becomes more like that of magnetite (Pherhat et al., 2007). Gold NPs (synthesized via citrate reduction) have a charge of around −55 mV (Kim et al., 2009), presumably due to citrate acid adsorbed on the surface. Multiwall carbon nanotubes (MWCNTs) treated with a mixture of sulfuric acid and nitric acid (3:1) together with ultrasonication have a zeta potential around −55 mV (Kim and Sigmund, 2004) due to carboxylation of the surface of the MWCNTs (Smith et al., 2009). Brant et al., Cheng et al., and Chen et al. have shown that stable fullerene clusters with negative charge of approximately −40 to −80 mV (from pH 2 to 12) were formed from mixing fullerene clusters in water for a period of several weeks (Brant et al., 2005; Chen and Elimelech, 2009; Cheng et al., 2004). The nature of these charges is under investigation. These examples demonstrate that core-shell structures, the presence of coatings, and chemical transformations impart charges to NP surfaces. These charge sources, or combinations thereof, are not accounted for in colloid science. Understanding the fate of NPs in the environment therefore requires a fundamental comprehension of the types of transformations that the NPs may undergo during manufacturing, under commercial use, and after release into the environment (as discussed later in this review).

**Complex Crystal Structures**

Complex NP crystal structures can present challenges to colloid science because changes in the crystal structure can alter Hamaker constants and surface charges in ways not explainable by theory. Additionally, defects in the crystal lattice can alter surface charge (Evans and Wennerstrom, 1999; Israelachvili, 1991). The crystal structure of materials with the same atomic composition can play a large role in determining surface charge. Nano-sized TiO2, for example, has three different polymorphs: rutile, anatase, and brookite, each with a unique crystal structure. The zeta potential is approximately −20 mV (French et al., 2009) when anatase and brookite structures are predominant and is approximately −35 mV (Lebrette et al., 2004) when the rutile phase is predominant (both measured at pH 7.5). This is consistent with findings that the dielectric constant can be altered by annealing pure anatase-phase TiO2 to the rutile phase (Kim et al., 2005). The Hamaker constant is a function of dielectric constant (Tabor and Winterton, 1969); therefore, the Hamaker constant also can depend on the crystal structure of NPs. This is important to consider for NP systems containing mixtures of phases or where crystal structures are altered for applications, such as photocatalysis with TiO2.

**Shape**

In DLVO modeling, one of the primary assumptions is that particles are spherical. This assumption is reasonable for ideal latex particles and some ideal colloidal systems. Manufactured NPs, however, come in a variety of nonspherical shapes. Triangles, icosahedrons, ellipses, rhombohedrons, spindle, rod, and tube shapes are possible (AgNPs [Moon et al., 2009], FeO3NPs [Wang et al., 2009], and AgS [Ma et al., 2007]), thereby complicating traditional DLVO and XDLVO.

Both vdW and EDL forces are affected by changes in shape. Several researchers have investigated these changes (Bhattacharjee and Elimelech, 1997; Montgomery et al., 2000; Vold, 1954). At a separation distance smaller than the mean diameter (∼ρ1/3, where ρ is the volume of particles), the attraction between anisometric particles, such as plates, rectangular rods, and cylinders, is larger than for spherical particles of equal volume because a greater number of atoms are in close proximity (Vold, 1954). The attraction between spheres, rods (and cylinders), and platelets varies as ρ−1, ρ−2, and ρ−3, respectively, where ρ is separation distance (Vold, 1954). For cylindrical particles, parallel orientation is energetically favored over a perpendicular orientation at small distances. For rectangular rods or platelets, an orientation with the largest faces opposite each other is the most favorable energetically. Electrostatic double-layer forces of cylindrical particles are theoretically a function of particle orientation (Vold, 1954). These results imply that shape can theoretically control aggregation under some favored orientations. For example, Kozan et al. (2008) studied the aggregation of tungsten trioxide (WOx) nanowire suspensions of different types (uneven, single, or bundled in
diameter) and dimensions (diameter of 40–200 nm and nominal lengths of 2, 4, 6, and 10 μm) in various polar solvents and compared the aggregate morphology of the nanowires with that of spherical WO₃ NPs (40 nm in diameter) (Kozan et al., 2008). The aggregates of spherical WO₃ NPs were more compact and more spherical in shape (Dₐ ~ 2.6 and Rₐ ~ 3.8 μm) than aggregates of nanowires with diameter of 200 nm (Dₐ ~ 2.3 and Rₐ ~ 2.2 μm). Moreover, aggregation of the nanowires for 7 d in a quiescent environment resulted in no significant Rₐ increase but an increase in Dₐ (Kozan et al., 2008). This reorganization is related to the predicted behavior that anisometric particles are likely to aggregate under a secondary minimum (Vold, 1954). The degree of secondary minimum aggregation is dependent on shape and is most favorable for platelets, less favorable for rods and cylinders, and least favorable for spherical NPs (Vold, 1954). Loose aggregates formed in the secondary minimum might gradually restructure into denser aggregates in the primary minimum. Nanoparticles designed with a myriad of unique shapes (Cai and Sandhage, 2005; Kawano and Imai, 2008; Sanchez-Iglesias et al., 2009) therefore challenge colloid science to understand their aggregation behavior in the environment because of the model complexity of understanding these shapes in a DLVO framework. Although nonconventional theories, such as surface element integration (Bhattacharjee and Elimelech, 1997), may account for interfacial forces in irregular shapes (e.g., ellipsoids), these theories are difficult to apply to the unique (e.g., helical) and diverse types of nanomaterial shapes.

### Table 2. Examples of surface coated nanoparticles and their applications.

<table>
<thead>
<tr>
<th>Particle type</th>
<th>Surface modifier</th>
<th>Purpose</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantum dots</td>
<td>amphiphilic alkyl-modified polyacrylic acid</td>
<td>alter particle hydrophilicity and modify quantum dot interactions with other biological compounds</td>
<td>Luccardini et al. (2006)</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>polyacrylic acid</td>
<td>stabilize dispersions and modify surface chemistry allowing attachment of an antibody for a substrate selective photocatalytic system</td>
<td>Kanehira et al. (2008)</td>
</tr>
<tr>
<td>Fe²⁺/Fe-oxide</td>
<td>poly(styrene sulfonate), polyaspartate, carboxymethyl cellulose, or triblock copolymers</td>
<td>inhibition of aggregation, decreasing adhesion to solid surfaces, increasing mobility in the subsurface, and targeting specific pollutants</td>
<td>He et al. (2009), Kanel et al. (2008), Phenrat et al. (2008), Phenrat et al. (2009c), Phenrat et al. (2009a), Saleh et al. (2005)</td>
</tr>
<tr>
<td>Carbon nanotubes</td>
<td>various kinds of anionic, cationic, nonionic surfactants and polymers</td>
<td>individually stabilized, single-walled carbon nanotubes</td>
<td>Moore et al. (2003)</td>
</tr>
<tr>
<td>Silver</td>
<td>daxad 19 (sodium salt of a high-molecular-weight naphthalene sulfonate formaldehyde condensate)</td>
<td>stabilize dispersions silver nanoparticles</td>
<td>Sondi et al. (2003)</td>
</tr>
</tbody>
</table>

### Table 3. Examples of surfactant properties and their relationship to particle stabilization.

<table>
<thead>
<tr>
<th>Property</th>
<th>Findings</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surfactant chain length</td>
<td>A linear relationship exists between the surfactant chain length and the logarithm of a surfactant necessary to disperse hydrophobic particles.</td>
<td>Dederichs et al. (2009)</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>Stabilization of CNT‡ with nonionic surfactants increased with molecular weight (e.g., Brij 78 [MW = 1198 g mole⁻¹] stabilized 4.3% of CNT, while Brij 700 [MW = 4670 g mole⁻¹] could stabilize 6.4% of CNT)</td>
<td>Moore et al. (2003)</td>
</tr>
<tr>
<td>Type of ionic head groups</td>
<td>At similar molecular weight, cationic surfactants such as dodecyltrimethylammonium bromide (MW = 308 g mole⁻¹) and cetyltrimethylammonium bromide (MW = 364 g mole⁻¹) were slightly more effective in stabilizing CNT than anionic sodium dodecylbenzenesulfonate (MW = 348 g mole⁻¹).</td>
<td>Moore et al. (2003)</td>
</tr>
<tr>
<td>Self-assembly structure</td>
<td>Sodium dodecyl sulfate, anionic surfactant, forms cylindrical micelles as helices or double helices and hemiellular structures on CNT. Random adsorption of surfactants on CNT hypothesized to enhance stabilization of the CNT dispersions.</td>
<td>O’Connell et al. (2002), Richard et al. (2003), Yurekli et al. (2004)</td>
</tr>
</tbody>
</table>

‡ CNT, carbon nanotube.

### Surfactants and Macromolecular Surface Coatings

Nanomaterials are commonly manufactured with surface coatings (e.g., surfactants, polymers, and polyelectrolytes) to enhance dispersion stability or to provide specific functionality (He et al., 2007; Hezinger et al., 2008; Hydutsky et al., 2007; Mayya et al., 2003; Phenrat et al., 2008; Saleh et al., 2008; Saleh et al., 2005; Zhang et al., 2002). Table 2 summarizes some examples of surface-coated NPs and their applications. Adsorbed or covalently bound surfactants prevent aggregation and enhance dispersion stability of NPs by increasing surface charge and electrostatic repulsion or by reducing interfacial energy between particle and solvent (Rosen, 2004). Coulombic attractions (Rosen, 2004; Vaisman et al., 2006; Wang et al., 2004), hydrophobic interactions (Vaisman et al., 2006), and surfactant concentration (Vaisman et al., 2006) affect the adsorbed surfactant mass and layer conformation and hence the ability of a surfactant to stabilize a NP against aggregation. Table 3 summarizes the properties of surfactants that affect their ability to stabilize NPs against aggregation. Low-molecular-weight surfactants reversibly adsorb on particle surfaces (Rosen, 2004), so, without a strong interaction between the surfactant and NP surface, the surfactant may desorb or be displaced by higher-molecular-weight natural polymers such as NOM when the particles are released into the environment. Therefore, changes in the stability of surfactant-coated NPs are expected on release to the environment.

Polymers are organic macromolecules consisting of repetitions of smaller monomer chemical units (Fleer et al., 1993).
They can be synthetic (e.g., polyethylene glycol) or naturally occurring (e.g., biomacromolecules, such as proteins and polysaccharides) (Brewer et al., 2005; Jain et al., 2005; Liu et al., 2006). They also are surface active agents but are generally of higher molecular weight than surfactants discussed previously. Unlike surfactants, the repeating monomer units can adsorb to NPs at multiple places along the polymer chain, making polymer adsorption stronger than surfactant adsorption and relatively irreversible. For example, Kim et al. (2009) modified NZVI by physisorption of various types of strong and weak polyelectrolytes and found that <30% by mass of polymer desorbed from the NPs over a period of 4 mo (Kim et al., 2009). Polyelectrolytes are charged polymers. Their charge is derived from ionizable groups built into the polymer structure (e.g., from -COO⁻, -SO₄⁻, or -SO₃⁻ groups) (Fleer et al., 1993). Adsorbed polymers and polyelectrolytes provide electrosteric repulsions that prevent NP aggregation. These repulsive forces have osmotic ($V_{osm}$) and elastic-steric ($V_{elas}$) components due to their charge and large molecular weight, respectively (Fig. 4). The magnitude of the electrosteric repulsion is governed by the surface excess (adsorbed mass of polymers per unit surface area of a NP), polymer molecular weight, polymer density, adsorbed layer thickness, and solution composition (see expressions in Table 1 and examples in Tables 4 and 5) (Fritz et al., 2002; Ortega-Vinuesa et al., 1996; Phenrat et al., 2008; Romero-Cano et al., 2001).

Surfactant–NP and polymer–NP interactions are extremely complex and often kinetically controlled rather than being in thermodynamic equilibrium. The science describing or predicting adsorbed mass and adsorbed layer conformation is immature, and the adsorbed mass and layer conformation depends on NP properties and solution conditions (pH, ionic strength, ionic composition). Therefore, predicting the effects of adsorbed surfactants, polymers, or polyelectrolytes on NP behavior in the environment is challenging.

**Effect of Nanoparticle Aggregation on Applications and Implications for the Environment**

Understanding NP aggregation under well controlled solution conditions in the laboratory is difficult because NP properties present challenges for colloid science. However, ultimately we would like to comprehend the fate, transport, reactivity, and risks associated with manufactured NPs released into the environment. How do these intrinsic challenges in understanding aggregation affect our understanding of NP fate, transport, and effects in more complicated environmental settings? Figure 5 summarizes some of the environmental interactions of NPs that affect or are affected by aggregation and are discussed next.

**Effect of Solution Chemical Composition on Aggregation: pH and Ionic Solutes**

pH and dissolved ionic solutes play crucial roles on aggregation of NPs in engineered and natural systems. These parameters can be controlled in laboratory settings but may vary spatially and temporally in natural systems. Spatial heterogeneity of minerals in the subsurface alters the concentration of ionic species present in different systems (e.g., groundwater versus surface water). Variation in aquatic environment pH stems from the same phenomenon. A better understanding of how pH and dissolved ionic solutes affect the behavior of organic macromolecule–coated NPs in the environment is needed. Surface charge titration and EDL screening are the two primary ways that pH and ionic solutes promote NP aggregation. Most NP surfaces have surface functional groups (e.g., hydroxide and oxide groups) that are titratable by H⁺ or OH⁻. Excess of H⁺ (low pH) normally results in a positively charged particle surface,

<table>
<thead>
<tr>
<th>Polymer property</th>
<th>Findings</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorbed layer thickness and surface excess</td>
<td>Correlate to dispersion stability of polymer modified Fe⁰–Fe oxide nanoparticles.</td>
<td>Phenrat et al. (2008)</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>Dispersion stability of carbon nanotubes increased as the molecular weight of Pluronic increased.</td>
<td>Moore et al. (2003)</td>
</tr>
<tr>
<td>Condition of polymer adsorption: heat treatment</td>
<td>Adsorption of polycrylic acid on TiO₂ enhanced at 150°C versus 20°C. This resulted in the enhanced dispersion stability.</td>
<td>Kanehira et al. (2008)</td>
</tr>
<tr>
<td>Condition of polymer adsorption: solvent property</td>
<td>More polycrylic acid adsorbed on TiO₂ in dimethylformamide than in water.</td>
<td>Kanehira et al. (2008)</td>
</tr>
</tbody>
</table>
Table 5. Examples of particle stabilization and destabilization by natural organic matter and biomolecules.

<table>
<thead>
<tr>
<th>System</th>
<th>Findings</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂ (positively charged) at pH 2 to 6 with 1 mg L⁻¹ FA†</td>
<td>Disaggregation of TiO₂, resulting in a smaller particle size (3 nm) than the original bare TiO₂ obtained from the manufacturer (10 nm).</td>
<td>Domingos et al. (2009)</td>
</tr>
<tr>
<td>TiO₂ (negatively charged) pH &gt; PZC with 1 mg L⁻¹ FA</td>
<td>Flocculation of TiO₂ due to bridging FA was observed. Aggregation decreased with increasing ionic concentration. High ionic concentration screened the negative charges of FA and TiO₂, resulting in greater FA adsorption onto TiO₂ promoting stabilization, not bridging.</td>
<td>Domingos et al. (2009)</td>
</tr>
<tr>
<td>C₆₀ or CNT with HA (CaCl₂ concentration &lt;40 mmol L⁻¹)</td>
<td>Humic acid as low as 1 mg L⁻¹ increased dispersion stability of C₆₀ up to 5 mg L⁻¹. Humic acid concentrations increased the dispersion stability of CNTs from 5 to 300 mg L⁻¹.</td>
<td>Chappell et al. (2009), Chen and Elimelech (2007)</td>
</tr>
<tr>
<td>C₆₀ with HA (CaCl₂ concentration &gt;40 mmol L⁻¹)</td>
<td>Unadsorbed HA aggregated through intermolecular bridging via calcium complexation. Aggregates subsequently bridged C₆₀, resulting in flocculation.</td>
<td>Chen and Elimelech (2007)</td>
</tr>
<tr>
<td>AuNPs with BSA</td>
<td>Gold nanoparticles coated with BSA were stable as colloids at the PZC of bare AuNPs, suggesting steric stabilization due to adsorbed BSA layers.</td>
<td>Brewer et al. (2005)</td>
</tr>
<tr>
<td>AuNPs with lysozymes</td>
<td>Enhanced aggregation of lysozyme–AuNP assemblies at physiological pH at very low lysozyme concentrations (16 nmol L⁻¹). Au nanoparticles were found embedded in the lysozyme matrix.</td>
<td>Zhang et al. (2009)</td>
</tr>
</tbody>
</table>

† AuNP, gold nanoparticle; BSA, bovine serum albumin; CNT, carbon nanotubes; FA, fulvic acid; HA, humic acid; PZC, point of zero charge.

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**Nanoparticle aggregation in the environment**

Fig. 5. Hypothesized effects of the environment on nanoparticle aggregation and how aggregation state could alter nanoparticle (NP) environmental interactions. (A) pH and ions. Increasing acidity can lead to charge neutralization at the point of zero charge. Increasing ionic strength reduces the size of the electrostatic double layer and repulsive forces. Certain ions (e.g., Ca²⁺) can bridge functional groups on the surface of nanoparticles. (B) Heteroaggregation. Macromolecules present in the environment coat nanomaterials leading to a steric effect. Larger macromolecules trap NPs in a mesh or gel causing stabilization or destabilization. Nanoparticles also associate with other particles such as clays or biocolloids. Nanoparticles flow through porous media depending on their aggregation state. (C) Biological interactions. Cells activate phagocytosis mechanisms depending on if a particle is aggregated or not. Nanoparticles containing metals aggregate at the surface of organisms and release metal ions at varying rates. (D) Transformations. Oxidants or sunlight degrade particle coatings or the particles themselves. Aggregated photoactive NPs only have the outside particles active.
whereas excess of OH⁻ (high pH) normally yields a negatively charged surface. For each particular system, the pH at which the H⁺ and OH⁻ concentration causes suspended particles to have a neutral charge is called the PZC. As pH moves toward this point, the EDL repulsion decreases, and aggregation is promoted by vdW attraction (Fig. 5A). Charge reversal (i.e., from negatively charged to positively charged particles) is also possible. This change would dramatically affect NP behavior because most surfaces in the environment are negatively charged at near neutral pH. As for the ionic species effect, high ionic concentration decreases the Debye length (Å⁻¹) (see Table 1 for calculation of EDL using DLVO), resulting in the decrease of the extent of EDL repulsion (Fig. 5A). The ionic concentration where the repulsive energy barrier is completely screened and rapid aggregation occurs is known as the critical coagulation concentration. Table 6 summarizes factors governing nanomaterial critical coagulation concentration and dispersion sensitivity toward electrolyte concentration. In many cases, surface titration and EDL screening effects occur in NP dispersions as they occur for large colloidal particles. However, there are notable exceptions where the pH_{PZC} depends on the NP size. Table 7 summarizes parameters altering nanoparticle PZC.

### Heteroaggregation and Deposition

The environment is a complex system with multiple primary molecules and particles as well as solution compositions. Straightforward DLVO theory is difficult to apply to these systems, and typically XDLVO forces are brought into models to improve results (Wu et al., 1999). At best, DLVO + XDLVO provides qualitative information about aggregation and deposition. Hence, aggregation and deposition processes need to be measured for each material and preparation method. Natural organic matter (NOM) in the environment can significantly alter the aggregation and deposition of NPs. Even without fully defined structure, due to its macromolecular nature, NOM is expected to prevent aggregation and deposition presumably due to electrosteric stabilization (Amirbahman and Olson, 1993; Amirbahman and Olson, 1995). Natural organic matter consists of mainly humic and humic substances. Fulvic compounds typically make up 40 to 80% of NOM compounds, and, due to their small size (~1 kDa), they can coat the surfaces of particles. Fulvic compounds alter the surface charge and have been shown to stabilize with an effect similar to surfactants (Domínguez et al., 2009). In fact, NOM may stabilize MWCNTs better than surfactants commonly used for laboratory suspensions of MWCNTs (Hyung et al., 2007). However, enhanced dispersion stability due to electrosteric forces and destabilization due to bridging have been experimentally observed, and it is not often possible to predict these interactions. Natural organic matter attaches to the surface of particles in a variety of ways. For example, irreversible adsorption onto the surfaces of iron oxide via ligand exchange between carboxyl/hydroxyl functional groups of humic acid and iron oxide surfaces (Gu et al., 1994) or hydrophobic interactions with carbon based nanomaterials (Hyung et al., 2007) have been reported. Whether or not attachment results in stabilization, but this information is useful for understanding the influence of various parameters on aggregation and deposition.

### Table 6. Factors governing nanomaterial critical coagulation concentration and dispersion sensitivity toward electrolyte concentration (ionic strength).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Findings</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of ionic species</td>
<td>Regardless of particle type, CCC† for divalent ions (e.g., CaCl₂ or MgCl₂) is lower than for monovalent ions (e.g., NaCl).</td>
<td>Chen and Elimelech (2007), Evans and Wennenstrom (1999), Saleh et al. (2008)</td>
</tr>
<tr>
<td>Particle size</td>
<td>Values of CCC increase with increasing particle size (e.g., CCC values of Fe₂O₃ with diameter of 12, 32, and 65 nm have CCCs of 45, 54, and 70 mmol L⁻¹ NaCl, respectively).</td>
<td>He et al. (2008)</td>
</tr>
<tr>
<td>Type of particles</td>
<td>The CCC of carbon nanomaterials such as fullerene appears to be higher than that of metal oxide such as Fe₂O₃ (e.g., CCC of C₆₀ [dp = 60 nm] is around 120 mmol L⁻¹ NaCl, whereas that of Fe₂O₃ [dp = 65 nm] is 70 mmol L⁻¹ NaCl).</td>
<td>Chen and Elimelech (2007), He et al. (2008)</td>
</tr>
<tr>
<td>Particle shape</td>
<td>The CCC of carbon nanotubes is lower than C₆₀ particles. Van der Waals attraction is greater and EDL repulsion is lower for rod-like shapes than for spherical shapes.</td>
<td>Chen and Elimelech (2007), Saleh et al. (2008)</td>
</tr>
<tr>
<td>Surface modifier</td>
<td>Due to steric repulsion, polymorphic surface modification decreases the sensitivity of aggregation induced by ionic species. NZVI (dp = 162 nm) modified by guar-gum prevented aggregation at ionic concentrations up to 0.5 mmol L⁻¹ TiO₂ modified by PAA prevented aggregation in ionic concentrations up to 0.5 mol L⁻¹ NaCl.</td>
<td>Kanehira et al. (2008)</td>
</tr>
</tbody>
</table>

† CCC, critical coagulation concentration; EDL, electrostatic double layer; NZVI, nano zero valent iron; PAA, polyacrylic acid.

### Table 7. Parameters altering nanoparticle point of zero charge.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Findings</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical composition</td>
<td>PZCs of metal NPs,† metal oxides, and carbon nanomaterials have a wide range and need to be measured for each material and preparation method.</td>
<td>Brant et al. (2005), Kim et al. (2009), Kosmoluk (2009), Sirk et al. (2009)</td>
</tr>
<tr>
<td>Surface modification</td>
<td>Surface modification using anionic polyelectrolytes shifts PZC toward lower values (e.g., ~3 pH units for Fe⁺/Fe-oxide nanoparticles).</td>
<td>Kim et al. (2009), Sirk et al. (2009)</td>
</tr>
<tr>
<td>Particle size</td>
<td>PZCs for hematite nanoparticles of diameter 12, 32, and 65 nm are ~7.5, 7.8, and 8.5, respectively.</td>
<td>He et al. (2009)</td>
</tr>
<tr>
<td>Particle transformation</td>
<td>Aged Fe⁺/Fe-oxide nanoparticles have lower PZC than fresh NPs by ~3 pH units, presumably due to surface oxidation and hydrolysis.</td>
<td>Kim et al. (2009)</td>
</tr>
</tbody>
</table>

† NP, nanoparticle; PZC, point of zero charge.
lization or destabilization depends on several factors, including type of NOM, NOM concentration, and solution chemistry (Chen and Elimelech, 2007; Chen et al., 2006; Diegoli et al., 2008; Domingos et al., 2009). Stabilization usually results from NOM forming a charged stabilizing layer on the outside of the particle. Destabilization, on the other hand, results from particles being bridged by larger NOM molecules, such as rigid biopolymers (Fig. 5B, left). This occurs for relatively large-sized NOM (~10–100 kDa) and can dominate interactions between nanoparticles (Buffe et al., 1998). Large-molecular-weight biomolecules and biomacromolecules, including proteins, polypeptides, and amino acids (McKeon and Love, 2008; Moreau et al., 2007; Vamunu et al., 2008), affect aggregation of NPs in aquatic environments similarly. Table 5 summarizes reports of NP stabilization and destabilization afforded by the presence of NOM and biomacromolecules reported in literature.

**Nanoparticle Interaction with Inorganic and Biocolloids**

Nanoparticles released to the environment can interact with inorganic colloids (e.g., clays, aluminosilicates and iron oxyhydroxides) and biocolloids (e.g., bacteria), altering the dispersion stability of engineered NPs via heteroaggregation (Fig. 5B). Heteroaggregation with bacteria can prevent aggregation or promote disaggregation of NPs. Cerium oxide NPs were reported to attach the surface of bacteria at the maximum adsorption capacity of 15 mg of CeO₂ m⁻² due to electrostatic attraction (Thill et al., 2006). Holden et al. (2009c) showed that TiO₂ NPs were disaggregated in the presence of microorganisms (unpublished data). Heteroaggregation of NZVI and bacteria also increases dispersion stability when compared with dispersions containing no bacteria (Li et al., 2010). Heteroaggregation with bacteria, NOM, or mobile colloids (e.g., clay particles) could enhance NP stability, but heteroaggregation to large enough particles could also destabilize NP dispersions. A complete understanding of the impacts of heteroaggregation on NP behavior requires more experimentation.

**Effect of Aggregation on Deposition and Sedimentation**

Aggregation of NPs affects their fate and transport in ground and surface waters (Fig. 6). In the subsurface, aggregation affects deposition processes; in surface waters, aggregation drives sedimentation processes. Homoaggregation of NPs mostly leads to
high deposition rates in porous media because of increased col-
sions between NP clusters and aquifer materials via sedimenta-
tion and interception as opposed to relying only on Brownian motion. For example, NZVI injected into the subsurface at high
core concentration (1–10 g L−1) aggregate rapidly, and their
mobility in the subsurface suffers as a result (Kanel et al., 2008;-
Phenrat et al., 2007; Saleh et al., 2007) (i.e., they do not trans-
port far from their injection point).

There are numerous studies that suggest prevention of
aggregation improves transport in porous media. Polymeric
surface modification has been used to decrease NZVI aggrega-
tion and therefore deposition (Kanel et al., 2008; Kim et al.,
2009; Phenrat et al., 2009c; Phenrat et al., 2008; Saleh et al.,
2008). He et al. (2009) and Tiraferrri and Sethi (2009) observed
enhanced mobility of NZVI modified with adsorbed carboxy-
methyl cellulose and guar gum (He et al., 2009; Tiraferrri and
Sethi, 2009). Phenrat et al. (2009a) demonstrated that NZVI
transport was limited specifically by NP aggregation during
transport in porous media by comparing the transport of non-
aggregating hematite NPs and aggregating NZVI of the same
size and surface chemistry. When NP deposition is interpreted
by classical filtration theory (i.e., assuming no aggregation
during particle transport in porous media), the effect of aggre-
gation is neglected and can lead to error in the reported attach-
ment coefficient. This makes comparisons between different
experiments and systems difficult.

In contrast to homoaggregation, heteroaggregation with
mobile, natural colloidal particles (e.g., clay) and with natu-
ral particles that have low density (e.g., microorganisms) can
enhance transport of NPs in porous media by decreasing the
particle collision rate. For example, the presence of 20 mg
L−1 NOM enhanced NZVI transportability in porous media
(Johnson et al., 2009). Clay particles were also used as NZVI
supports to enhance NZVI mobility (Hydutsky et al., 2007),
which indicates that heteroaggregation between clay and NZVI
enhances NZVI mobility.

In surface waters, homoaggregation can enhance sedimen-
tation if aggregates or agglomerates reach a size where gravity
forces acting on the particles becomes significant compared
with Brownian diffusion (O’Melia, 1980). Nanoparticles with
low dispersion stability therefore tend to accumulate in the
sediment near their source (Fig. 6). Heteroaggregation, with
low-density natural colloids, may facilitate stabilization or dis-
aggregation of NPs, which would increase their residence times
in water bodies (Fig. 6). Stabilizing or destabilizing NPs against
aggregation can have far-reaching effects. For example, cerium
oxide NPs stabilized with surfactant remained dispersed as col-
lloids and were not effectively removed by an activated sludge
system (Limbach et al., 2008). Additionally, the removal effi-
ciency of functionalized versus nonfunctionalized fullerene
NPs by alum coagulation was compared. Increased steric sta-
bilization by surface functionalization prevented aggregation
and attraction with alum flocs (Hyung and Kim, 2009). In con-
trast, surface coatings, such as Tween 20 on SiO2 NPs, have been shown to enhance their flocculation and removal
during water treatment, whereas uncoated SiO2 NPs were not
removed (Jarvie et al., 2009). The ability to predict the aggrega-
tion effects of adsorbed or grafted organic macromolecular
coatings on NP surfaces is not possible with current DLVO
or XDLVO theory and is an important area of environmental
nanotechnology research.

Effect of Aggregation on Nanoparticle Reactivity
and Effect of Reactivity on Aggregation State

Aggregation can alter NP reactivity, and NP aggregation state
be altered by chemical or photochemical environmental
processes (Fig. 5D). Several types of NPs are photoactive
(e.g., C60 quantum Dots, and TiO2) and can produce reactive
oxygen species (ROS). A relationship between Df and photoac-
tivity indicates that the structure of the aggregates formed has a
role in determining ROS production and subsequent reactivity.
Fullerene (C60) is a photoactive carbon-based class of NP that
forms crystalline aggregates in water with high Df (i.e., closely
packed aggregates). This aggregation promoted triplet–triplet
annihilation and self-quenching due to close contact between
cages and severely reduced the quantum yield of C60 (Hotze
et al., unpublished data). Fullerol (hydroxylated fullerene),
which has a lower theoretical quantum yield than C60 produced
greater amounts of ROS than C60 under identical solution con-
tions because fullerol formed aggregates with lower Df (less
closely packed fractal aggregates), which decreased the amount
of triplet–triplet annihilation and increased ROS yield relative
to C60 (Hotze et al., unpublished data).

Aggregation has been shown to decrease the rate of dissolu-
tion of lead sulfide (PbS) NPs (Liu et al., 2008). The dissolution
rate of 240 nm aggregates of PbS NPs (4.7 × 10−10 mol m−2
s−1) was an order of magnitude lower than for monodisperse
14-nm primary PbS NPs (4.4 × 10−9 mol m−2 s−1) and also lower than for micrometer-sized particles of the same materi-
als. In addition to aggregation decreasing available surface area
for dissolution, they attributed the retarded dissolution to inhi-
bition in the highly confined space between the particles in
the aggregates. In confined space, water molecules arrange dif-
ferently than in the bulk, increasing viscosity at the interface.
Enhanced viscosity in confined space decreases the diffusion
rate of water to the surface and therefore the dissolution rate.
They also hypothesized that the overlap of the diffusion layer
between two adjacent particles in an aggregate can reduce the
concentration gradient (i.e., the driving force for dissolution)
from NP surfaces to bulk solution.

Another example of aggregation decreasing NP reactivity
is the dechlorination of carbon tetrachloride (CT) by 9-nm-
diameter magnetite NPs (Vikesland et al., 2007). The CT
dehlorination rate decreased as the degree of aggregation
of the magnetite NPs increased. By promoting aggregation
through addition of different concentrations of monovalent or
divalent cations, an inverse relationship between aggre-
gate size (measured by DLS) and the CT dechlorination rate
was established.

Although aggregation can affect NP reactivity, NP reactiv-
ity can also affect aggregation. Clusters of C60 also undergo
photochemical oxidation and subsequent disaggregation in
water (Hou and Jafvert, 2009; Lee et al., 2009). For exam-
ple, Hou and Jafvert (2009) reported that the photochemical
transformation of aqueous C60 clusters in sunlight decreased
mean aggregate size from 500 to 160 nm and produced unidentif-
data soluble reaction products after 65 d of exposure.
to natural sunlight (Hou and Jafvert, 2009). Lee et al. (2009) observed similar transformations under UV light exposure (Lee et al., 2009). Photochemical transformations of C_{60} also took place during heteroaggregation with NOM (Li et al., 2009) and enhanced the dispersion stability of NOM-coated C_{60} in comparison to nonilluminated samples (Li et al., 2009). Enhanced dispersion appeared to be due to a surface erosion or dissolution-recrystallization process catalyzed by sunlight, rather than a simple breakage of C_{60} from clusters (Li et al., 2009). Therefore, NPs designed to be reactive under photoilluminated conditions (e.g., C_{60} or TiO_{2}) could have their aggregation properties altered by long-term sunlight exposure.

Chemical oxidation could act in a similar manner by altering surface coatings or the underlying NP so that the particles gain or lose stability against aggregation (Fig. 5D). For example, ozone reacts with C_{60} (Fortner et al., 2007) and CNTs, breaking the carbon cage structure and altering the stability of the NPs against aggregation in aqueous suspension. This ozonation process has been demonstrated to render the oxidized C_{60} more photoactive than its unoxidized parent aggregates (Cho et al., 2009). Additionally, surfactants and coatings are susceptible to these same types of oxidation processes possibly decreasing the stability of NPs in the environment due to loss of the stabilizing coating. A better understanding of the biological and abiotic reactions affecting NP stability against aggregation is needed to predict their fate in the environment.

Effects of Aggregation on Biological Impacts from Nanoparticles

Aggregation of NPs can alter their biological effects by affecting ion release from the surface, if and where particles collect inside an organism, and the reactive surface area of NPs (Fig. 5C). Calculation of metal flux at cell surfaces is important for determining the bioavailability and ecotoxicity of nanomaterials. This is especially true in the case of silver NPs where silver ion release plays an important role in the inhibition of bacterial growth (Tàurozzi et al., 2008; Ju-Nam and Lead, 2008). Iron ion release may also prove to be important for determining the impacts of quantum dots and iron NPs, among others. Heteroaggregation can confound understanding of metal flux because the metal can also bind to surfaces and internal sites of naturally occurring colloids of various sizes and compositions (Buffl e et al., 2007). Solution chemistry (e.g., ionic strength and the amount and type of NOM) controls the fractal dimension of NP aggregates, with lower D_f (1.3–2.0) formed in solutions with high NOM, and higher D_f (2.3–2.7) formed in solutions without significant NOM present (Zhang et al., 2007). Aggregate structure plays an important role in how metal ions diffuse inside of the flocs where the kinetics of metal association and dissociation from binding sites is slowed by orders of magnitude compared with rates expected for free ions in solution (Buffl e et al., 2007). Understanding mechanisms by which aggregate structure affects the dissolution and release of ions and resulting ecotoxicity (e.g., from silver NPs) will improve insights into the potential impacts of such particles in the environment.

Aggregation alters the NP size distribution, in turn affecting the fate of NPs in biological systems as well as their toxicity. For example, 20-nm NPs were found to deposit mostly in the alveolar region, whereas 5- to 10-nm particles deposited in tracheobronchial region, and particles smaller than 10 nm accumulate mostly in the upper respiratory tract (Heyder et al., 1986; Oberdorster et al., 2007; Swift et al., 1994). This indicates that aggregation can alter exposure locations or exposure pathways. Nanoparticle aggregation was also shown to affect the mode of cellular uptake of NPs and subsequent biological responses. For example, phagocytosis by macrophages and giant cells is a mechanism used by cells to clear particles of a few microns or less (Oberdorster et al., 2007). Phenrat et al. (2009b) found that aggregation affected uptake of bare and polymer-modified NZVI particles by mammalian glial cells. Although the primary particle sizes of bare NZVI particles (20–100 nm) are smaller than the optimal size range (1–2 μm) for phagocytosis, the NZVI loosely aggregated to micrometer-sized clusters in the physiological buffer, triggering phagocytosis and subsequent uptake. Biological effects, therefore, vary depending on whether or not a particle is aggregated, among other confounding factors (e.g., endotoxins, adsorption of biomacromolecules, etc.). Given this fact, understanding aggregation in biological systems is essential for elucidating mechanisms of toxicity.

Conclusions

The ability to manipulate atoms allows scientists to create NPs with significantly different reactivity than their micro-sized analogs (He et al., 2008; Kanehira et al., 2008). Reports on NP behavior and effects to date indicate that the aggregation behavior of the NPs will significantly affect their fate, transport, reactivity, bioavailability, and effects in environmental systems. Fortunately, the science of aggregation is well developed. Unfortunately, the translation of that science into the regime of nanomaterials remains a challenge due to their unique physical and chemical properties (e.g., size, shape, composition, and reactivity). The presence of organic macromolecular coatings on NPs including those engineered as part of the NP, or those that are acquired in the environment (e.g., adsorption of NOM), further complicate analysis of NP behavior by traditional colloid science. Nanomaterial aggregation studies, therefore, aim to take into account how these types of novel surface properties will alter what is already understood about aggregation science. Ultimately, this will guide scientists’ grasp of how nanomaterials and NPs will occur in and affect environmental systems. Much work remains to gain a full understanding of NP aggregation and how to apply these principles to create better applications and lower impacts of nanomaterials.

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