

CHAPTER II

THEORETICAL DESCRIPTION OF INTERACTIONS IN NANOMATERIAL SUSPENSIONS

Chapter Overview

The process of electrophoretic deposition (EPD) has two steps: (1) electrophoresis, during which charged colloids are driven by an electric field toward the field-emanating surface, and (2) deposition, during which the particles collect on the electrode yielding a solid deposit. Successful deposition of materials via EPD imposes several requirements on the colloidal system to be used. First, the suspended particles need to have a net charge or dipole moment, or be highly polarizable compared to the solvent in which they are suspended, enabling them to be driven by the applied electric field to the deposition site. In order to get a smooth, homogeneous deposit, the suspension needs to be stable, meaning that it is, in part, free of large, rigid aggregations of the colloids. Particles can be prevented from aggregating through electrostatic or steric repulsion. This chapter discusses the origin of charge in colloidal nanomaterials, suspension stability, the competing attractive and repulsive interactions in a colloidal system and how these are manifest in the nanomaterial suspensions being investigated.

2.1 Charging of Colloidal Nanomaterials

Charges on nanomaterials arise from one or a combination of the following: deviations in stoichiometry, adsorption and desorption of surface ligands, dissolution of ions from the particle, and adsorption of ions from the solvent [8, 21, 22]. In aqueous environments, the addition of salt (e.g. $\text{KCl} \rightarrow \text{K}^+$ and Cl^-) or acid (source of H^+), for example, yields free ions that can adsorb to colloids. Alternately or additionally, surface functional groups such as carboxylic acids can dissociate resulting in charged moieties. In nonpolar media, such as hexane, the origin of charges on colloidal nanomaterials is not readily apparent. Because we investigated EPD phenomena using ligand-capped nanoparticles in hexane suspension, the discussion in this section will expand on the mechanism for ligand-mediated charging.

Prior studies of colloidal nanoparticles, using electrophoretic mobility measurements, show that the net charge on the particle can vary as a function of ligand composition and quantity. For example, the addition of oleic acid to PbSe nanocrystals shifted their charge in the positive direction, but replacing the oleic acid with tri-n-octylphosphine oxide (TOPO) yielded negatively charged nanocrystals [23]. This observation can be explained by the nature of the bonds that form at the surface. In the case of both ligands, they bond to the metal atom. It is probable that the hydrogen of the carboxylic acid partially screens surface electrons of Se while the bonding of the ligand creates a slight positive charge on the ligand. In contrast, TOPO contributes further lone pair electrons to the nanocrystal surface, explaining the negative charging that is observed. Figure 2-1 illustrates these ligand bonds.

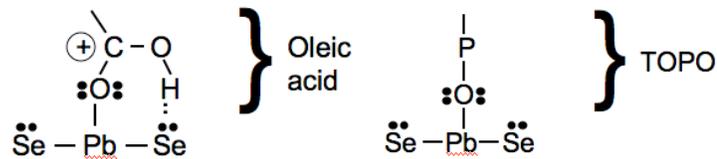


Figure 2-1. Diagram of the probable bonding of oleic acid and TOPO ligands at the surface of a PbSe nanocrystal.

In many EPD studies, the nanocrystals are “washed” in precipitation/re-suspension steps prior to the deposition step, resulting in the loss of ligands from the nanocrystal surface. Charge states are observed to evolve as a result. There is also evidence for thermal charging and the regeneration of charged nanocrystal populations, even after they are depleted during an EPD run [24]. Studies of CdSe deposited from hexane reported that ~ 1% of the nanocrystals are charged in ambient conditions [25]. Regarding thermal charging, when Boltzmann statistics are used to estimate the percentage of nanocrystals that are charged, the model does not distinguish between electrons and holes. In other words, the charged population is likely to be evenly split between negatively and positively charged nanocrystals. This calculation is in agreement with the observations reported in [25] and observed in our laboratory.

2.2 Stable Suspensions

In this section, we define what a stable suspension is for the purpose of doing EPD. Solid particles tend to aggregate due to the van der Waals forces between them. Colloidal stability is a measure of how well the system resists the particle aggregation, keeping particles dispersed individually in the suspension.

Sedimentation and flocculation are destabilizing mechanisms. Sedimentation results from gravity acting on the suspended particles. The downward motion of sedimentation can be countered by the upward diffusion of particles due to Brownian motion. If sedimentation overcomes Brownian motion, the particles can be prevented from settling by external agitation, such as stirring of the suspension. Flocculation results from particle-particle attractive van der Waals forces. As particles pass near each other, they can aggregate irreversibly. The aggregate of particles is called a floc, which can remain in the bulk of the suspension rather than sinking to the bottom of the container. This aggregation between particles can be prevented by electrostatic repulsion due to charges on the particles and by steric repulsion due to a coating layer of molecules or polymers that prevents the particles from coming close enough to aggregate. In the next section, we review the theory for assessing the stability of a suspension by calculating the energy of interaction between two particles in the suspension.

2.3 DLVO Theory

DLVO theory, named for Derjaguin, Landau, Verwey and Overbeek, provides the framework to determine the stability of a colloidal system by calculating the potential energy of a colloid. The net energy is the sum of attractive and repulsive interactions between particles and the interaction with the solvent. At particle separation on the order of nanometers, the contribution from the solvent is minimal [26], so here we focus on the interactions between particles. The classical DLVO formulation accounts for attractive van der Waals interaction and repulsive electrostatic interaction. These interactions are considered for the general case of spherical nanoparticles. Because we studied nanoparticles with organic ligand layers, we also

incorporated the effect of repulsive steric interactions. Where appropriate, we describe how the interactions are modified for the specialized case of sheet-like particles.

2.3.1 Attractive Interactions

While magnetic or electric dipole-dipole interactions can contribute to attraction between particles, at nanometer distances, attraction between particles is due primarily to the van der Waals (dispersion) force, which originates from fluctuations of electric dipoles in atoms. In the Hamaker theory, the van der Waals interaction between many-atom bodies is calculated as the sum of the interactions between pairs of atoms. Using integration, it is possible to calculate the van der Waals interaction for different geometries such as spheres, cylinders, and planes [27].

For two identical spherical bodies, the van der Waals interaction energy is given by the expression

$$U(d) = -\frac{A}{12} \left\{ \frac{2R^2}{d^2 + 2dR} + \frac{4R^2}{(d + 2R)^2} + 2 \ln \left[\frac{2d^2 + 4dR}{(d + 2R)^2} \right] \right\} \quad (2.1)$$

where A is the Hamaker constant, R is the body radius, and d is the surface-to-surface separation [28]. The Hamaker constant describes the induced dipole interaction of two materials interacting through a third medium. Negative values for the energy indicate attractive interaction. As an example, Figure 2-2 shows the van der Waals energy between two iron oxide nanoparticles in hexane ($A = 624 \text{ meV}$) [29], when both particles are 10 nm in diameter and when both particles are 14 nm in diameter. For a given combination of materials, the magnitude of the interaction energy scales with particle radius at small separations.

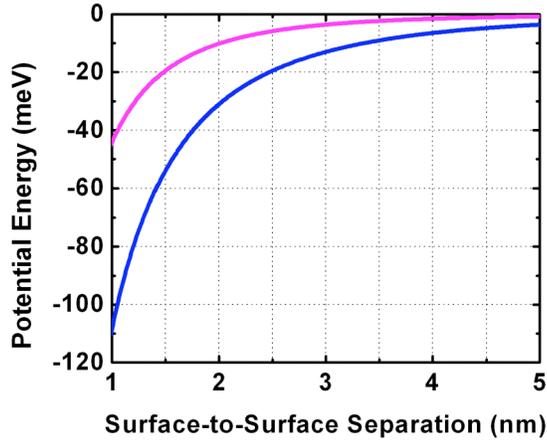


Figure 2-2. Energy of van der Waals interaction for two 10-nm iron oxide spherical particles (top, purple) and two 14-nm iron oxide spherical particles (bottom, blue).

The van der Waals interaction per unit area between two identical sheet-like particles with high aspect ratio, e.g. graphene oxide, can be approximated from the expression for the interaction between two planar surfaces,

$$\frac{U(d)}{area} = -\frac{A}{12\pi} \left(\frac{1}{d^2} + \frac{1}{(2t+d)^2} - \frac{2}{(t+d)^2} \right) \quad (2.2)$$

where A is the Hamaker constant, d is the surface-to-surface separation, and t is the sheet thickness [28]. If we examine extremely thin sheets at close separations ($t \rightarrow d$, on the order of < 1 nm), the expression in (2.2) reduces to

$$\frac{U(d)}{area} \approx -\frac{A}{20\pi d^2} \quad (2.3)$$

from which we see that van der Waals energy scales with $(1/d^2)$ for particles interacting face-to-face. Another group studying graphene oxide has asserted [30] that sheets interacting edge-to-edge, instead of face-to-face, have van der Waals energy scale with $(1/d^5)$, likening the geometry

to that of parallel chain molecules [27]. This is a reasonable assumption since an individual graphene oxide sheet is predominantly one atomic layer thick. If we plot the van der Waals interaction for two identical, 100 nm^2 graphene oxide sheets in water ($A = 14.8 \text{ meV}$) [31], we observe that the edge-to-edge interaction energy is negligible in comparison to the face-to-face interaction (Figure 2-3). (For the edge-to-edge interaction we assumed the sheets were $10 \text{ nm} \times 10 \text{ nm}$ squares, with the 10 nm edge of one sheet parallel to the 10 nm edge of the other sheet.)

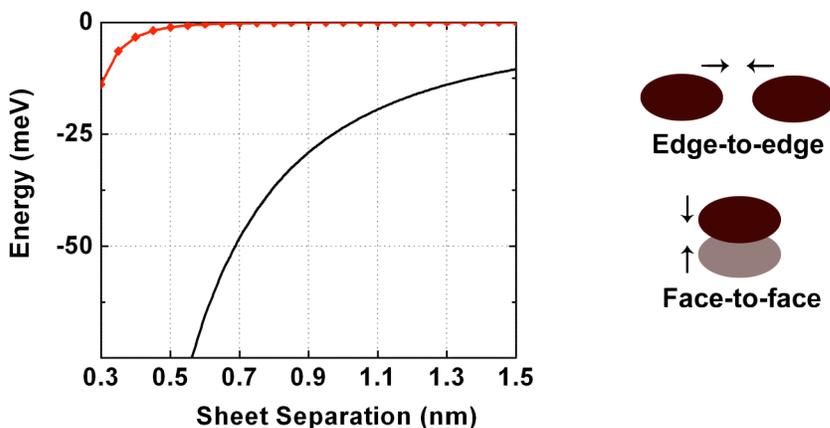


Figure 2-3. Energy of van der Waals interaction for two 100 nm^2 graphene oxide sheets interacting edge-to-edge (red, line with symbols) and for two 100 nm^2 graphene oxide sheets interacting face-to-face (black, line only).

The calculation methods described thus far were sufficient to understand the behavior we observed in our nanomaterial suspensions. Recently, it was shown that the calculation of the van der Waals interaction energy using the Hamaker theory becomes somewhat inaccurate when the particle separation is comparable to the particle size for cluster-like particles [32]. This condition is relevant to our setup of nanometer-scale particles and separation distances. The recently described “coupled-dipole method” models the van der Waals energy with greater accuracy by taking into account the positions of individual atoms in the particles. To improve our calculations further, one could harness greater computing power to implement the coupled-dipole method for our materials [33].

2.3.2 Repulsive Interactions

There are two repulsive interactions between colloids: electrostatic and steric.

Electrostatic interactions result from the charge on the colloids and the ions in solution. Steric interactions result from surfactant molecules located on the colloid surface. The mechanisms for each type of interaction are detailed below.

To describe the electrostatic interaction, we begin by examining a positively charged colloid in a bulk medium containing both positive and negative ions. In this environment, there will be a fixed layer of negative ions at the colloid surface. This is the Stern layer. Beyond the Stern layer, there are still more negative ions than positive ions because the former are attracted to the particle while the latter are repelled by it. This region is called the diffuse layer because the ions surrounding the particle are mobile compared to those in the Stern layer. With increasing distance from the particle, the concentration of negative ions comes to equal the concentration of positive ions, since the bulk medium is electrically neutral. Figure 2-4 shows the distribution of ions around a colloid. Collectively, the Stern layer and the diffuse layer constitute the electrical double layer around the colloid.

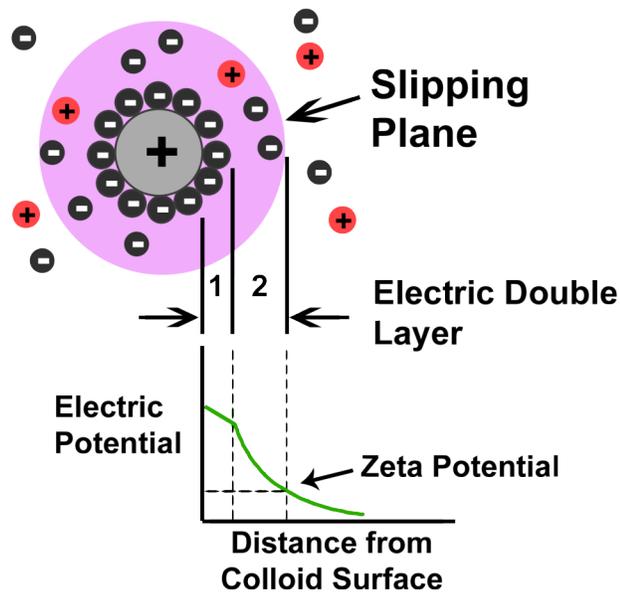


Figure 2-4. Distribution of ions around a colloid. 1: Stern layer, 2: Diffuse layer. The electric potential decreases with increasing distance from the colloid surface. The zeta potential, which is the electric potential at the slipping plane, is a special value that can provide information about the extent of electrostatic interaction between colloids and colloidal stability.

If two identically charged colloids are brought near each other in the presence of their double layers, they will not repel each other as strongly as they would if there were no double layers. This phenomenon, charge screening, reduces the magnitude of the particle-particle Coulomb interaction. However, if the concentration of ions in the double layer is high enough, then the double layers of the particles will collide, increasing the electrostatic repulsion. In order to calculate the energy of the Coulomb interaction between colloids with double layers, we need a method to characterize the charge surrounding the colloids.

The charge distribution around colloidal particles can be established by measuring their electrophoretic mobility. Electrophoretic mobility (μ) is measured by tracking the velocity (v) of colloidal motion in response to an applied electric field (E). (See Appendix A for information on the instrument used to measure mobility.) The relationship among these quantities is given in Equation (2.4).

$$\mu \equiv \frac{v}{E} \quad (2.4)$$

Let us consider again the positively charged colloid, surrounded by the Stern layer and diffuse layer of ions. In response to the applied electric field, the colloid moves towards the negatively polarized surface. Some of the negative ions in the diffuse layer, however, move in the opposite direction because they are repelled by the negatively polarized surface. Within the diffuse layer, a boundary exists, inside of which the negatively charged ions move with the colloid. This boundary is called the slipping plane. Thus, a measurement of electrophoretic mobility assesses the motion of the colloid and its ions within the slipping plane, as this motion is impeded by flow in the opposite direction due to ions outside the slipping plane.

The electrostatic potential at the slipping plane is called the zeta potential. Zeta potential is the most useful metric for the strength of colloid charge because it accounts for the ions inside the slipping plane and it is related to a measurable quantity, the electrophoretic mobility. Zeta potential (ζ) is related to mobility (μ) by the expression

$$\zeta \equiv \frac{1.5\mu\eta}{\epsilon f(\kappa a)} \quad (2.5)$$

where η is the dynamic viscosity of the solvent, ϵ is the dielectric permittivity of the solvent, and $f(\kappa a)$ is the Henry function. The value of the Henry function depends on both the Debye length (κ^{-1}) and the particle radius (a). The Debye length describes the screening length of a suspension (solvent and ions); the expression for Debye length is

$$\kappa^{-1} = F^{-1} \left(\frac{2c}{\epsilon RT} \right)^{-1/2} \quad (2.6)$$

where F is the Faraday constant, c is the concentration of monovalent ions, ϵ is the dielectric permittivity of the solvent, R is the molar gas constant, and T is the thermodynamic temperature [34]. Typical values for the Debye length are ~ 1 nm for a 0.1 M NaCl solution and ~ 960 nm for pure water. In our experiments with purified hexane, the Debye length was expected to be quite high, in the vicinity of 1000 nm [23]. If the particle size is small compared to the Debye length ($\kappa a \rightarrow 0$) the Henry function equals 1 (Hückel approximation). If the particle size is large compared to the Debye length ($\kappa a \rightarrow \infty$) the Henry function equals 1.5 (Smoluchowski approximation). By applying Equations (2.3) and (2.4) and the appropriate approximation for the Henry function to a mobility measurement, we can calculate the zeta potential of that colloidal system. The magnitude of the zeta potential is associated with differing degrees of colloidal stability; typically, 30 mV is the threshold above which colloids are considered stable and not prone to aggregation [26].

With the zeta potential of the colloidal system known, it is possible to calculate the energy of the electrostatic repulsion using the expression

$$U(rep) = 2\pi\epsilon a \zeta^2 e^{-\kappa D} \quad (2.7)$$

where a is the particle radius, D is the particle separation, ζ is the zeta potential, and κ is the inverse of the Debye length. Thus, we see that the repulsion energy for a given particle separation increases as the magnitude of the zeta potential increases, and decreases as the ionic strength of the suspension is increased because of the decrease in the Debye length due to increased charge screening.

The other kind of repulsive interaction, steric repulsion, results from the presence of ligand molecules or polymers on the surface of a colloid. Steric repulsion is an entropic effect; as the colloids are brought closer, the number of possible ligand conformations is reduced. For nanoparticles, steric repulsion helps to prevent them from aggregating irreversibly due to van der Waals forces. Using a soft sphere model, the steric repulsion energy can be modeled as

$$U(\text{steric}) \approx \frac{100 R \delta^2}{(r-2R)\pi\sigma^2} kT \exp\left(\frac{-\pi(r-2R)}{\delta}\right) \quad (2.8)$$

where r is the center-to-center separation, R is the particle radius, δ is the ligand length, and σ is the diameter of the area each ligand covers on the particle surface [35]. We did not need to calculate steric repulsion for the graphene oxide sheets because they lacked a ligand layer. However, if one desired to use a sheet with a ligand covering, the calculation could be performed using the de Gennes model for brush layer interaction between two plates with adsorbed polymer layers [36]. In the de Gennes model, from which Equation (2.8) was derived, the steric repulsion energy scales with $(1/r^{5/4})$ at small separation distances.

2.3.3 Total Interaction Energy

The overall energy of interaction, accounting for the interactions described previously, was calculated for the 14 nm iron oxide nanoparticles with oleic acid ligands that were suspended in hexane for the subsequent EPD work. It is plotted in Figure 2-5 as a function of surface-to-surface separation of a pair of particles. The energy barrier indicated in the figure prevents the nanoparticles from aggregating. The electric field applied during EPD supplies the energy to overcome this barrier. The well depth to the left of the energy barrier is ~ 60 meV, more than twice the magnitude of $k_B T$ at room temperature, ~ 26 meV. The relative depth of this well suggests that nanoparticles brought in close proximity by EPD will remain adhered to each other.

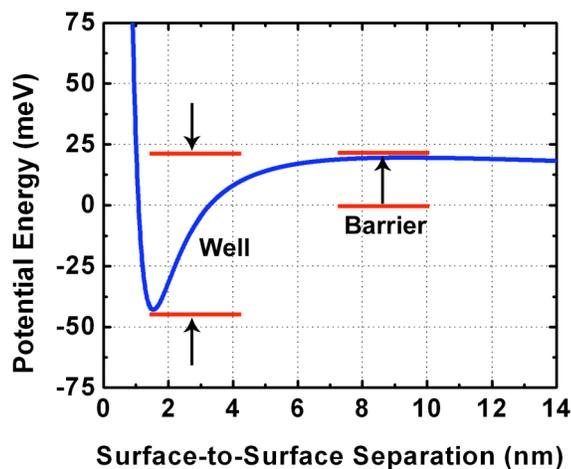


Figure 2-5. Total interaction energy between two 14-nm iron oxide nanoparticles in hexane.

With the graphene oxide sheets dispersed in water, we planned to tune the suspension stability by modifying the ion concentration, which in turn changes the zeta potential. In Figure 2-6, we plot the calculated total interaction energy for a pair of identical 100 nm² sheets using different zeta potential conditions. One pair of sheets has zeta potential magnitude 35 mV (black, open symbols) and one pair of sheets has zeta potential magnitude 15 mV (red, closed symbols). The energy barrier to aggregation is quite high for the sheets at 35 mV zeta potential, in excess of 150 meV. We would expect these sheets to form a stable suspension with no aggregation. In contrast, the sheets at 15 mV zeta potential exhibit a small energy barrier to aggregation, less than 20 meV. We would expect these sheets to aggregate at room temperature.

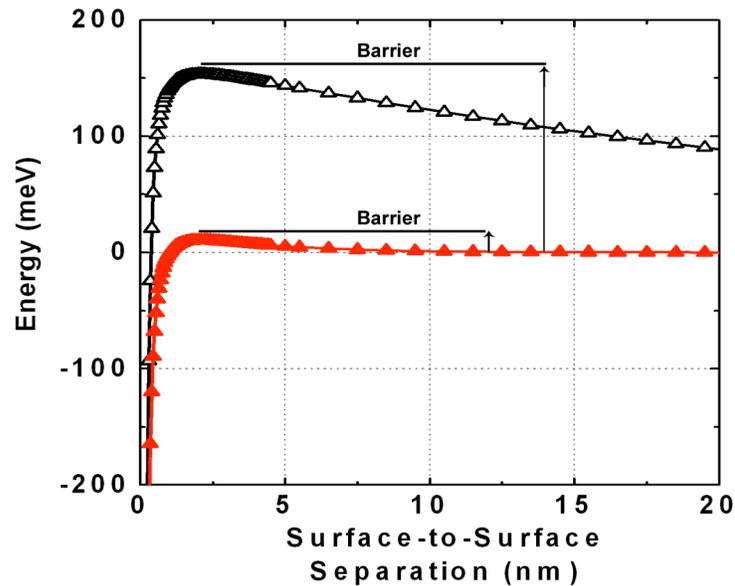


Figure 2-6. Total interaction energy between two identical 100 nm² graphene oxide sheets in water with zeta potential magnitude 35 mV (black, open symbols) and between two identical 100 nm² graphene oxide sheets in water with zeta potential magnitude 15 mV (red, closed symbols).

In this chapter, we have shown how to assess the stability of a suspension by using DLVO theory to calculate the interaction energy between two particles in the suspension. In stable suspensions, there is an energy barrier that prevents aggregation of the particles. In the next chapter, we review the mechanisms of EPD that enable particles to form a solid deposit, either by driving the particles to overcome the repulsive force associated with the energy barrier or by altering the local charge concentration to lower the energy barrier.