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Chemical Principles of Nanoengineering



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To Bo, Delia, & Jon and to all the students of NANO 102.

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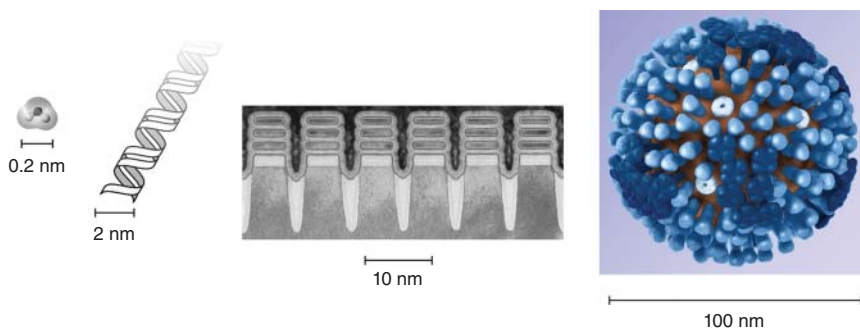
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Introduction

What is Nanoengineering?

If you were to look up the definition of “nanoengineering,” it might read something like this: *Nanoengineering is an engineering field that seeks to control materials and processes on the scale of 1–100 nm*. While accurate, this doesn’t exactly clarify what a nanoengineer does... and with good reason. If we think about the type of objects we might categorize as being nanoscale, we see that:



- A water molecule is around 0.2 nm.
- A human DNA strand is around 2.5 nm wide.
- A transistor on a computer chip is approximately 10 nm in size.
- A flu virus is around 100 nm in diameter.

Thus, while we might be able to clearly define the length scale that nanoengineering deals with, it is much more difficult to pinpoint the types of problems that nanoengineers might tackle. Nanoscale materials and processes affect a wide swath of technologies. As a result, nanoengineering is an inherently interdisciplinary field of engineering, with implications in chemistry, biology, electronics, and medicine.

What is clear, however, is that things behave differently at the nanoscale than what we encounter in our macroscopic world. If you drop a ceramic cup on the floor, it is likely to shatter into many smaller pieces. At the nanoscale, a piece of ceramic

can bend and twist and be tied into a neat little bow as readily as a piece of ribbon. Chitin is a sugar-like biomolecule that, in our macroscopic world, is a boring beige color. When it is molded into nanoscale patterns like those found in a butterfly wing or into nanoscale layers like those found in a beetle exoskeleton, chitin is a brilliant blue or shimmery gold. This is the result of how light interacts with chitin at the nanoscale.

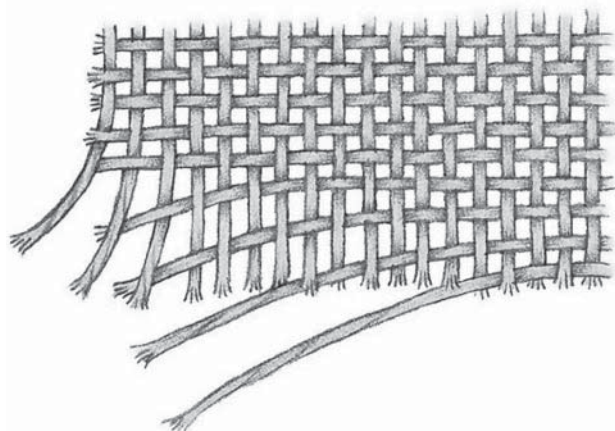


To observe these nanoscale phenomena, we need specialized tools to “see” what is happening. For example, a light microscope that we would typically find in a science classroom is useful for visualizing the detail of small objects such as an onion cell or a human hair. These microscopes provide a magnification of around 1000 times. To see nanoscale objects, however, we employ electron microscopes that use a beam of electrons to illuminate objects, such as nanoribbons and butterfly wings. Electron microscopes magnify these objects around 10 000 000 times. To probe even smaller features, we shine neutrons and X-rays onto an object. And for the many nanoscale objects that are too small or the nanoscale processes that are too fast to observe experimentally, we have computational models that help us “see” all that is going on. Because such tools are continuously improving, our ability to engineer nanoscale materials and processes is also improving.

Because nanoengineering is a relatively new and continuously evolving discipline, you may find it bewildering to try and define what the work of a nanoengineer might entail. But this is also the promise of nanoengineering: *to create new inventions that disrupt and change the way we approach technology*. You are stepping into new territory.

What are Chemical Principles of Nanoengineering?

The nanoscale (1 nm) is a hop, skip, and jump away from the atomic scale (1 Å). Because of this, nanoengineering involves the application of several principles that cross into the domain of chemistry. A few key concepts are outlined below.



Atomic structure and bonding: At the most fundamental level, nanoengineering requires an understanding of how atoms and molecules bond together. This is a guiding chemical principle for the design and discovery of new materials (nanoscale or otherwise), where atomic interactions lead directly to new and interesting properties. This is also a guiding principle for engineering *hierarchical materials*, i.e. materials that possess relevant features at multiple length scales. (Think of a silk sweater that is made of woven yarn, where the yarn is made of twisted fibers, where the fibers are made of connected silk strands, where the silk strands are made of silk protein chains, etc... this is hierarchy!). Structure and bonding at the atomic scale often provide the blueprint for structure and bonding at larger length scales.

Intermolecular forces: These are the attractive and repulsive forces that exist between molecules or particles of a substance, often dictating macroscopic properties, such as boiling point or solubility of a substance. Traditionally, chemical bonds (covalent, ionic, and metallic) are classified separately from the “physical bonds” that result from intermolecular forces. At the nanoscale, however, these physical bonds can be just as important (and just as strong) as a chemical bond. This is a guiding principle in the engineering of *supramolecular* (where there are many interacting molecules) and nanoparticle systems. This is also a guiding principle in the area of nanoscale self-assembly, where many molecules/objects are engineered to organize into a structure or pattern.

Surface and interfacial phenomena: A *bulk* property refers to the average property of a macroscopic chunk of material. A surface or interfacial property refers to a

property that is uniquely associated with the boundary regions between at least two types of materials (e.g. a solid particle suspended in a liquid). The surface of material can be drastically different from the bulk material in its chemical composition, atomic structure, and thermodynamics. While all materials that exist in our macroscopic world have surfaces and interfaces, their effects become much more pronounced for nanoscale objects. This is a guiding principle in the synthesis of nanomaterials and in the fabrication of nanoscale devices, where a single device (e.g. an electronic transistor or a chemical sensor) often involves the generation of many types of materials interfaces.

Who is this Book Intended for?

This book is not a technical manual, nor does it survey the wide world of nanomaterials and their chemical properties. This book is meant to teach the reader about fundamental scientific principles that intersect the fields of inorganic chemistry, physical chemistry, surface science, and solid-state physics. These fundamentals are taught through the lens of nanoengineering by asking the reader to apply the presented concepts and equations to nanoscale materials. Each chapter includes a list of approximately 20 tangible, numeric (or at least quantitative) problems for students to work through, with worked example problems included throughout each section.

This book was originally developed for an undergraduate course in the Nanoengineering Bachelor of Science degree program at the University of California, San Diego. Because of this, it was primarily written with two kinds of students in mind:

- Undergraduates majoring in engineering who are interested in nanoengineering and nanotechnology, but who have only dabbled in one or two advanced chemistry classes beyond general chemistry.
- Undergraduates majoring in chemistry who are interested in nanomaterials and have just started their trajectory into advanced materials chemistry (e.g. solid-state and polymers) courses.

Of course, this book may also serve as a useful introductory resource for many others, including graduate students embarking in nanoengineering and nanomaterials studies and those who simply wish to learn more about the nanoscopic world around them. To the reader, whomever you are, I offer the words of Dr. Seuss: “Your mountain is waiting, so... get on your way!”

According to the van der Waals theory, oil and water shouldn't separate and surfactants shouldn't form membranes, but they do . . . Such behaviors are crucial for life as we know it to exist.

—Jacob Israelachvili

1

Intermolecular Forces

In nanoscale systems, multiple chemical interactions are involved. For example, let us consider a dispersion of *nanoparticles*, shown in Figure 1.1. The glass vial in the image holds a liquid in which small solid particles (approximately 80 nm in diameter) are suspended. The nanoparticles shown in Figure 1.1 are composed of silver (Ag), which are known to exhibit special optical properties such as enhanced scattering and absorbance. The nanoparticles remain suspended in the liquid because they are coated with a layer of organic molecules, called polymers. What kinds of chemical interactions occur in this nanoscale system?

First, we can identify the chemical bonds that make up the different states of matter in the system. These include the bonds that hold the Ag atoms together within the core of the nanoparticle. Likewise, we can consider the chemical bonds within each molecule of liquid and any other molecules present in the system. *Interatomic* forces are responsible for the chemical bonds that hold atoms together to form molecules and solids. These include ionic, covalent, and metallic bonds – the so-called “strong” bonds. We will cover the formalization of these bonding models in later chapters. As we will find out, these bonds occur over short distances (a few angstroms) and are often highly directional.

But what about the chemical interactions that allow the nanoparticles to remain suspended in the liquid? What about the interaction between nanoparticles? Or the interaction between a molecule of liquid and a nanoparticle? Or between two molecules of liquid? *Intermolecular* forces are responsible for these “weak” or secondary bonds that occur between molecules, particles, and surfaces. The bonds that result from intermolecular forces lack specificity, stoichiometry, and directionality. These forces can also result in interactions that occur over long distances – much longer than interatomic bond lengths.

As we will see throughout Chapter 1, intermolecular forces play an important role in dictating materials and molecular behavior at the nanoscale. We will cover five different types of intermolecular forces: electrostatic, hydrogen bonding, van der Waals (vdW), hydrophobic, and steric forces. For each of these, we will derive and discuss their universal force laws. We will also discuss the differences between these forces for molecules versus nanoscale objects. Finally, we will develop an understanding of how potential energy diagrams can be used to predict the overall intermolecular interactions between two objects as a function of separation distance.

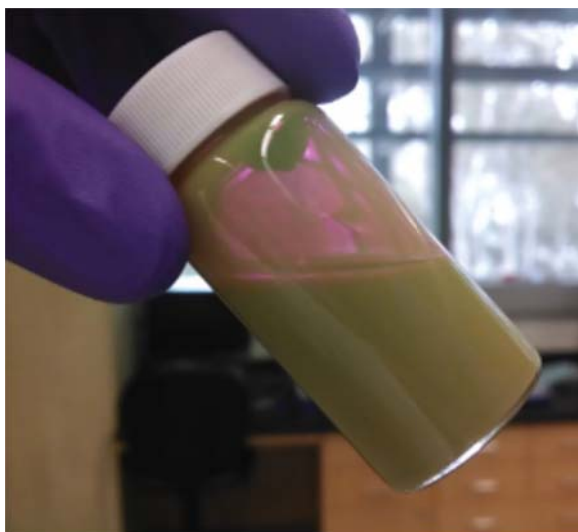


Figure 1.1 A vial of Ag nanoparticles suspended in liquid.

This knowledge will be applied toward understanding the behavior of nanosystems ranging from atoms and molecules (e.g. DNA and polymers) to particles and other nanomaterials (e.g. liposomes, metal nanoparticles, C_{60}).

1.1 The Pairwise Potential

Intermolecular forces can lead to attraction or repulsion between atoms, molecules, particles, and surfaces, and contribute significantly to how nanoscale materials and systems behave. These forces are classified as *conservative* forces, meaning that they satisfy the relationship:

$$F = -\frac{dV(r)}{dr} \quad (1.1)$$

where F is the force, $V(r)$ is the potential energy of the object, and r is distance. Because of this relationship, potential energy can be used as a descriptor of whether the force between two objects is attractive or repulsive.

We often consider *pairwise potentials* that describe $V(r)$ as a function of separation distance to determine attraction or repulsion. For example, two possible pairwise potentials between two spherical particles of radius R_s are depicted in Figure 1.2.

In a closed system, objects at equilibrium will move into a position that *minimizes the total potential energy*. Thus, in the pairwise potential on the left, the two objects repel each other since $V(r)$ becomes increasingly positive as the objects approach each other. In the pairwise potential on the right, the two objects attract each other since $V(r)$ becomes increasingly negative as the objects approach each other.

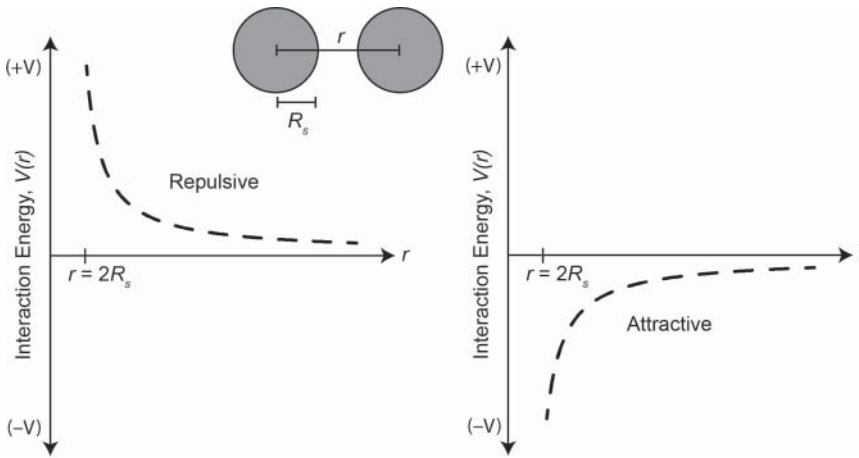


Figure 1.2 Examples of two pairwise potentials showing repulsive (left) and attractive (right) interactions between approaching spherical particles.

Worked Example 1.1

Question: Consider a volume of liquid-dispersed nanoparticles with separation distance, r , that behave according to the following pair potential:

$$V(r) = e^{-r/2}$$

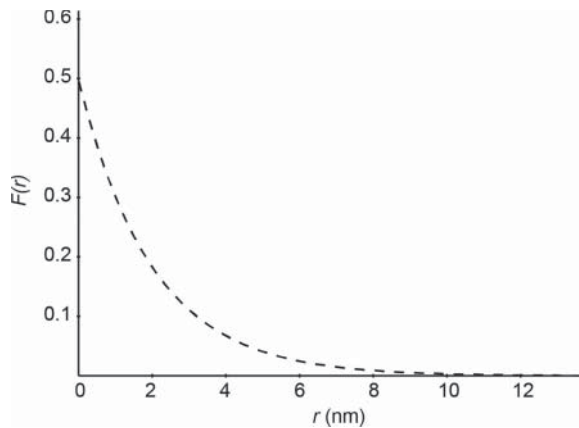
Plot the force curve for two approaching nanoparticles and determine whether you expect the nanoparticles to stay dispersed or aggregate in the liquid at room temperature.

Answer: First, we can derive the expression for the force between two approaching quantum dots:

$$F = -\frac{dV(r)}{dr} = -\frac{d}{dr} \left(e^{-r/2} \right) = \frac{1}{2} e^{-r/2}$$

Plotting $F(r)$ gives Figure 1.3:

Figure 1.3 Force curve.



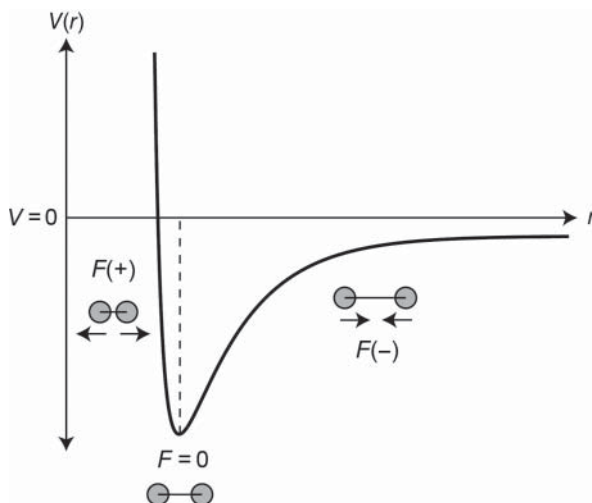


Figure 1.4 An example of a pair potential where the attractive and repulsive forces cancel each other out, leading to a potential well or energy minimum. The energy minimum in this plot corresponds to the equilibrium of the system.

Since $F(r)$ is always positive, the force between the nanoparticles is purely repulsive and increases in magnitude as $r \rightarrow 0$. Thus, we expect the nanoparticles to repel each other and remain dispersed in the liquid.

In most nanoscale systems, multiple intermolecular interactions contribute to the behavior of a given object. *Equilibrium* is achieved when the net force acting on the object is zero. Consider the pair potential shown in Figure 1.4. There is a strong repulsive potential for small values of r and a strong attractive potential at large values of r . At an intermediate value of r , the attractive and repulsive forces are perfectly balanced. Equilibrium is achieved at this energy minimum, where the slope of the pair-potential curve is equal to zero:

$$F = -\frac{dV(r)}{dr} = 0 \quad (1.2)$$

At equilibrium, a small perturbation of the system will result in the system being restored to the energy minimum. For example, consider what would happen if the two spheres at equilibrium were pulled apart and we increased r by a small amount: the negative force acting on the spheres would bring the spheres back toward each other and lower $V(r)$. Similarly, if we pushed the two spheres closer together and decreased r by a small amount, the positive force acting on the spheres would pull the spheres away each other and lower $V(r)$. For this reason, the energy minimum shown in Figure 1.4 is also referred to as the *stable* equilibrium or a *potential well*. Note that an equilibrium point corresponding to an energy maximum corresponds to an *unstable* equilibrium.

Worked Example 1.2

Question: Consider two nanoscale objects with a separation distance, r (in nm), and whose interaction energy is described by the following pair potential:

$$V(r) = -\frac{10}{r} + \frac{1}{r^3}$$

Determine whether or not the two objects can interact and reach a stable equilibrium and the separation distance for which equilibrium occurs.

Answer: First, we can recognize that the pair potential consists of an attractive term ($-10/r$) and a repulsive term ($1/r^3$). Equilibrium occurs when the forces associated with these two potential terms cancel each out.

$$\begin{aligned} F &= -\frac{dV(r)}{dr} = 0 \\ &= -\frac{d}{dr} \left(-\frac{10}{r} + \frac{1}{r^3} \right) = -\frac{10}{r^2} + \frac{3}{r^4} \end{aligned}$$

Thus, we can solve for r :

$$r = (3/10)^{1/2} \approx 0.55 \text{ nm}$$

The objects reach a stable equilibrium at $r = 0.55 \text{ nm}$ because this corresponds to a minimum in the potential energy diagram.

The pair potential discussed above provides a simple example of how we can use energy and force curves to understand how a nanoscale system will behave (e.g. whether it will be in or out of equilibrium). This will depend entirely on whether an interaction is repulsive or attractive, which in turn is dependent on the strength and distance dependence of each contributing intermolecular interaction. Table 1.1 lists the scaling laws for several different types of intermolecular forces. In the following sections, we will learn about these various intermolecular forces and their corresponding force and energy scaling laws.

1.2 Electrostatic Interactions

Electrostatic interactions, which are generated by the electric force between charges, account for a number of interaction geometries found in nanoscale systems. These include:

Table 1.1 General relationships between interaction geometries and separation distance.

Geometry of interaction	Type of interaction	Distance dependence
Ion-ion	Electrostatic	$1/r$
Ion-dipole	Electrostatic	$1/r^2$
Dipole-dipole	Electrostatic	$1/r^3$
Hydrogen bond	Electrostatic	$1/r^2$
Two atoms	van der Waals	$1/r^6$
Atom-surface	van der Waals	$1/r^3$
Sphere-sphere	van der Waals	$1/r$
Sphere-surface	van der Waals	$1/r$
Surface-surface	van der Waals	$1/r^2$

- ion pairs
- ion–dipole and dipole–dipole interactions
- dative bonds, where a molecule is coordinated to a metal center
- π – π bonding.

The electric forces in the above interactions are all governed by Coulomb's law, which states that for two bodies with charges Q_1 and Q_2 and separated by a distance, r , the potential energy of interaction is:

$$V(r) = \frac{Q_1 Q_2}{4\pi\epsilon\epsilon_0 r} \quad (1.3)$$

The corresponding electric force is given by:

$$F = -\frac{dV(r)}{dr} = \frac{-Q_1 Q_2}{4\pi\epsilon\epsilon_0 r^2} \quad (1.4)$$

where the constant ϵ is the relative permittivity of the medium surrounding the bodies and ϵ_0 is the vacuum permittivity. Note that Q_1 and Q_2 can be designated as positive or negative, where like charges are repulsive (resulting in a positive $V(r)$) and unlike charges are attractive (resulting in a negative $V(r)$). *Permittivity* can be thought of as the charge capacitance of a material, where a material with a large ϵ value is able to store more of the electric field. A medium with a high permittivity decreases the electrostatic force that is generated from Q_1 and Q_2 since it can more effectively screen the two charged bodies from each other.

Worked Example 1.3

Question: Calculate the interaction potential for a Na^+ ion and Cl^- ion in water with a separation distance of 100 and 0.1 nm. At 20 °C, water has a relative permittivity of $\epsilon = 80.2$.

Answer: Each ion has a charge of $+/- e$. Plugging this into Coulomb's law, we get

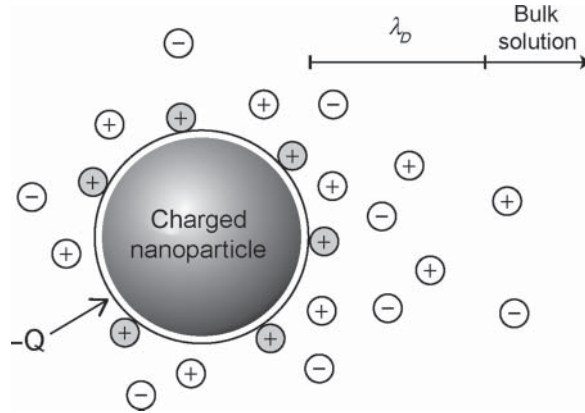
$$\begin{aligned} V(r) &= \frac{Q_1 Q_2}{4\pi\epsilon\epsilon_0 r} = \frac{(+1)(-1)(1.602 \times 10^{-19} \text{ C})^2}{4\pi(80.2) \left(8.85 \times 10^{-12} \frac{\text{C}^2}{\text{J} \cdot \text{m}}\right) r} \\ &= \frac{-2.88 \times 10^{-30} \text{ J} \cdot \text{m}}{r} \\ &= -28.8 \times 10^{-24} \text{ J for } r = 100 \text{ nm} \\ &= -28.8 \times 10^{-21} \text{ J for } r = 0.1 \text{ nm} \end{aligned}$$

It can sometimes be helpful to look at binding energies in units of kJ/mol to compare these values to average bond energies:

$$\begin{aligned} V(r) &= -0.017 \frac{\text{kJ}}{\text{mol}} \text{ for } r = 100 \text{ nm} \\ V(r) &= -17 \frac{\text{kJ}}{\text{mol}} \text{ for } r = 1 \text{ nm} \end{aligned}$$

For comparison, the covalent Cl—Cl bond in Cl_2 is ~ 240 kJ/mol, over one order of magnitude higher than the binding energy for our electrostatic interaction at 0.1 nm.

Figure 1.5 Schematic of a spherical particle with a uniform shell of negative charge immersed in an electrolyte solution.



Electric fields that occur in a medium containing free charges (e.g. blood or electrolytes such as a salt solution) undergo electrostatic screening. For example, consider a spherical nanoparticle with surface charge, $-Q$, shown in Figure 1.5.

In an electrolyte solution, such as an aqueous solution of NaCl, the ionic charge distribution near the nanoparticle surface becomes much more concentrated compared to the bulk electrolyte. Positively charged ions (e.g. Na^+) are attracted to the negatively charged nanoparticle, causing an increase in ion concentration near the nanoparticle surface. The mobile charges in the electrolyte effectively reduce the overall electric field generated by the charged nanoparticle. The screened electric field decays exponentially according to the following relationship:

$$V(r) = V_0 e^{-r/\lambda_D} \quad (1.5)$$

where the term λ_D is called the Debye length and r is distance from the nanoparticle surface. λ_D is a characteristic persistence length for the electrostatic effect and can be calculated using the formula:

$$\lambda_D = \sqrt{\frac{\epsilon \epsilon_0 k_B T}{2 N_A e^2 \sum c_i z_i^2}} \quad (1.6)$$

where e is the elementary charge, i is the number of different types of ions, c is the concentration of each ion, and z is the valence of each ion. An electrolyte such as an aqueous solution of NaCl is considered symmetric (since the number of Na^+ ions is equal to the number of Cl^- ions) and monovalent (since $z = 1$ for both ions). For a solution of NaCl, the formula for λ_D can be simplified to:

$$\lambda_D(\text{m}) = \sqrt{\frac{\epsilon \epsilon_0 k_B T}{2 N_A e^2 C}} \quad (1.7)$$

where C is concentration of the dissolved NaCl in molar units (M). Thus, we see that both an increase in the electrolyte concentration and an increase in the ion valence serve to reduce λ_D and more effectively screen electrostatic interactions. Debye lengths for standard electrolyte solutions tend to be between 1 and 100 nm. Because

the dimensions of nanomaterials are on the order of these Debye lengths, electrolyte concentration can have a profound impact on the electrostatic interactions of nanomaterials.

Worked Example 1.4

Question: Calculate λ_D for a nanoparticle dispersed in 1 and 10 mM aqueous solutions of NaCl, and compare the screened electric field, $V(r)$, for both cases.

Answer: We can plug this electrolyte concentration directly into the formula for λ_D :

$$\begin{aligned}\lambda_D(\text{m}) &= \sqrt{\frac{\epsilon\epsilon_0 k_B T}{2N_A e^2 C}} \\ &= \sqrt{\frac{(80.2) \left(8.85 \times 10^{-12} \frac{\text{C}^2}{\text{J} \cdot \text{m}}\right) \left(1.38 \times 10^{-23} \frac{\text{J}}{\text{K}}\right) (293 \text{ K})}{2(6.02 \times 10^{23})(1.602 \times 10^{-19} \text{ C})^2 \left(\frac{10^{-3} \text{ mol}}{\text{l}}\right) \left(\frac{10^3 \text{ l}}{\text{m}^3}\right)}} \\ &= 9.6 \times 10^{-9} \text{ m} = 9.6 \text{ nm for 1 mM NaCl}\end{aligned}$$

Similarly, we can plug in $C = 10 \text{ mM}$ to obtain $\lambda_D = 3.0 \text{ nm}$. We can compare the electric field potentials for the two concentrations by plotting $V(r)/V_o$ as a function of distance (Figure 1.6).

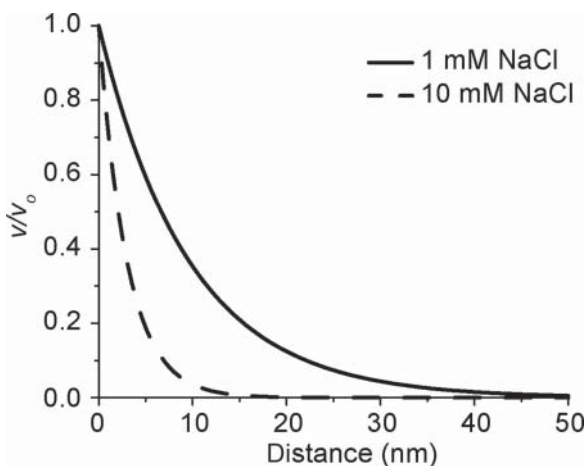


Figure 1.6 Change in electric field potential for varying electrolyte concentration.

We see that for 10 mM NaCl, nanoparticle charge will be more effectively shielded and the electric field decays much closer to the nanoparticle surface. Note that the Debye length is only dependent on the medium and not the properties of the nanoparticle.

In many nanoscale systems, we must consider the additive effects of multiple pairs of electrostatic interactions. For example, the total binding energy of an *ionic solid* – a material held together almost entirely through electrostatic ionic bonds – can be

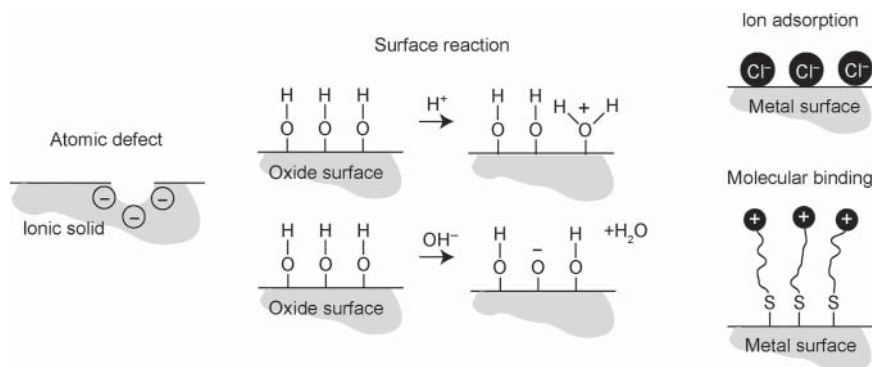


Figure 1.7 Three examples of how surface charge can be generated on nanostructures.

calculated by summing up all of the ion-pair potentials in the solid. If we wanted to calculate the binding energy in 1 M of table salt (NaCl), we could do so by summing up all ion-pair potentials involving Na^+ and Cl^- ions in the NaCl crystal lattice. Note that this would include both the electrostatic interactions for attractive Na^+/Cl^- pairs and repulsive Na^+/Na^+ and Cl^-/Cl^- pairs.

We can also use summation to calculate how electrostatic interactions contribute to the overall binding energy between two charged nanostructures or nanoparticles. However, we must take two major differences into consideration. First, nanostructures are not point charges. Unlike ions such as Na^+ , nanostructures possess dimensions that approach the Debye length of most media. Second, many nanostructures are not composed of a charged material, but rather possess a net surface charge. Surface charges can arise due to various mechanisms as shown in Figure 1.7, including:

- Atomic defects at the surface
- Adsorption of ions onto the surface
- Adsorption or binding of molecules with functional groups that are charged
- Chemical reactions that occur at the surface (e.g. acid/base reactions).

For nanostructures where surface charges are isotropically (i.e. uniformly) distributed over its surface, it is convenient to describe the surface charge density, σ , given by:

$$\sigma = \frac{\sum q}{A} \quad (1.8)$$

where $\sum q$ is the total net charge distributed over a surface area, A (Figure 1.8).

Thus, a nanoparticle that possesses a net surface charge density, σ , can be treated like a uniform shell of charge $\sum q$.

Worked Example 1.5

Question: Consider an Au nanoparticle with a diameter, $d = 30 \text{ nm}$, that is negatively charged due to adsorbed citrate ions (Figure 1.9).

The citrate ion can be approximated as a sphere with radius $r = 3.6 \text{ \AA}$. Estimate the overall net charge, Q , and the surface charge density, σ , for the Au nanoparticle.