Assembling nanocrystal superstructures

Marino, E.

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It’s a dangerous business, Frodo, going out your door. You step onto the road, and if you don’t keep your feet, there’s no knowing where you might be swept off to.

— J.R.R. Tolkien

Optoelectronic devices based on semiconductors are widespread and satisfy the energetic needs of modern society: From solar cells to power our homes, to light-emitting diodes to provide lighting, to transistors to compose our computers, semiconductors have shaped the world in the last 50 years. Yet, novel approaches are needed to fabricate cheaper and more efficient devices. In this introductory chapter, I will describe the fundamental principles at the basis of nanotechnology, and the advantages thereof. Using a top-down approach, I will proceed from a semiconductor single crystal to a nanocrystal, and highlight the novel properties that arise at the nanoscale, and how we can use them to target the technological needs that classical approaches may not satisfy. Further, I will describe the colloidal properties of semiconductor nanocrystals, and the different pairwise interactions we can exploit to fabricate novel, artificial solids.
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1.1 Going nano

1.1.1 Setting the stage

Modern society relies heavily on semiconductors: Light-emitting diodes provide lighting for our environments, solar cells power our homes and transistors compose our computers. Life as we know it would not exist without semiconductors. This is truly surprising when considering that less than a century ago, Wolfgang Pauli expressed his frustration with the understanding of semiconductor physics at the time:

*One should not work on semiconductors. They are a mess. Who knows whether semiconductors exist at all.* (1931) [1]

This pessimistic scenario dramatically shifted with the development of a clear theory of semiconductors that can successfully explain and predict the physics exploited in devices. Yet, novel effects develop when semiconductors become very small. How small? This thesis is concerned with the optoelectronic properties of semiconductors at extremely small scales when compared to our daily lives: The unit scale of this small world is 0.000000001 meters, or 1 nanometer. To give the reader a ballpark of how small a nanometer is, the printed full stop at the end of this sentence is about 300000 nanometers wide. The suffix *nano* is routinely used to describe objects and effects at this particularly small scale. What makes this scale so special?

1.1.2 Motivation of this thesis

Crystalline semiconductors of nanometric dimensions are known as semiconductor nanocrystals. Usually, the electronic properties of semiconductors do not depend on size; this changes at the nanoscale. For the last 30 years, the size-dependent optoelectronic properties of nanocrystals have fascinated scientists. From a fundamental point of view, nanocrystals provide a text-book example of the particle-in-a-box problem, allowing the investigation of novel quantum effects. [2][3] From a more practical perspective, these nanostructures are relevant to the development of novel optoelectronic devices and present several advantages against bulk semiconductors.

It is well known that the chemical composition of a semiconductor determines its bandgap. Consequently, alloying has been employed successfully to tune the bandgap of a semiconductor, a typical example being In$_{1-x}$Ga$_x$As where the bandgap can be varied between 0.36 and 1.43 eV. The use of nanocrystals completely removes this limitation by introducing a size-dependent bandgap: For instance, the bandgap of CdSe nanocrystals can be tuned continuously between 1.7 and 3.1 eV, the whole visible spectrum, by simply changing the nanocrystal size. [4] The physical origin of this effect is exclusively quantum, and therefore absolutely general. [5]
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Changing the bandgap of a semiconductor is of interest to solar applications, where thermodynamics poses a severe limit to the power conversion efficiency of a single bandgap device, known as the \textit{Shockley-Queisser} limit.\[6\] Losses result mainly from photons with energy \(\hbar \omega\) lower or much higher than the bandgap \(E_g\). In the former case, light is not absorbed; in the latter, the excess energy \(\hbar \omega - E_g\) is lost as heat during thermalization of charge carriers. Using a tandem device employing multiple sub-cells varying in bandgap decreases these losses by providing a better match to the solar spectrum while complicating device architecture.\[7\] Yet, nanocrystals can provide a simple and unique solution to reduce thermalization losses: Multiple exciton generation. Through this process, the absorption of a single photon of energy \(nE_g\) can generate \(n\) thermalized excitons.\[8\] These excitons can then be separated by applying an electric field to yield \(n\) free electrons, to obtain an external quantum efficiency of \(n \times 100\%\).\[9\]

A size-dependent bandgap implies a size-dependent emission spectrum. This has immediate consequences for lighting applications, allowing to fabricate a white light-source by employing a single material and three different sizes of nanocrystals.\[10\] Furthermore, the discrete density of states makes nanocrystals naturally suited as gain medium in lasing applications.\[11\]

Nanocrystals also present structural advantages against bulk semiconductors. While bulk semiconductors are brittle, nanocrystals can be deposited as thin films on flexible substrates, providing a low-cost and scalable solution to future wearable electronics.\[12\] Furthermore, the fabrication methods of bulk semiconductors traditionally rely on slow and expensive high-temperature processes, such as the \textit{Czochralski} method, tailored for single-crystal growth. Instead, nanocrystals can be synthesized via quick and inexpensive chemical methods,\[13\] representing the ideal building blocks for the miniaturization of optical components.

However, one of the main hurdles to the implementation of any application lies in the reproducible assembly of nanocrystals into close-packed superstructures. Advances in this regard have so far been limited by our understanding of interparticle interactions at the nanoscale. With the intent of bridging this gap, this thesis investigates the driving forces of nanocrystal assembly and the resulting superstructures. To provide the reader with a sufficient theoretical background to appreciate the content of this thesis, in this chapter we will explore the fundamentals of semiconductor nanocrystals and the pairwise interactions that govern their assembly at the nanoscale.

1.1.3 From bulk to nano

Bulk semiconductors are characterized by two sets of closely-spaced electronic states: One of these is entirely filled with electrons, and is known as the \textit{valence band}; the other one, instead, is entirely empty, and is known as the \textit{conduction band}.\[14\] These two bands are separated by an energy gap, \(E_g\), where no electronic states are
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present: The bandgap. An electron excited to the conduction band can recombine by emitting a photon of energy equal to the bandgap. These properties are intrinsic to the material, and generally do not depend on size. However, the quantum effects arising from restricting the motion of charge carriers to nanoscale volumes fundamentally modify the energetic structure of the material, imposing discrete valence and conduction bands. Importantly, the energy of the available electronic states, the value of the bandgap, and therefore light absorption and emission properties, all become intrinsically dependent on the degree of confinement. In the next sections we will review the physical origin of these properties of matter at the nanoscale, deriving from the so-called quantum confinement effect.

1.1.4 The quantum confinement effect

Consider a perfect and infinite crystal of semiconductor material. Then, according to Bloch’s theorem, an electron excited across the bandgap can travel freely and his motion is described by a wave function \( \psi \), that is the product of a plane wave and a function \( u \) with the same periodicity as the crystal:

\[
\psi(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u(\mathbf{r})
\]

where \( \mathbf{r} \) and \( \mathbf{k} \) are vectors in the real and reciprocal space, respectively. Suppose now to be able to carve out a small volume from the infinite crystal, of average linear dimensions \( \sigma = (\sigma_x, \sigma_y, \sigma_z) \); let the crystalline order inside the volume to be unaffected by the carving and the outer surfaces be perfectly reflecting for electrons. For simplicity, we first consider the motion of the electron along the x-axis. Heisenberg’s uncertainty principle states that if we confine a particle to a region \( \Delta x \) in space, this introduces an uncertainty in its momentum given by:

\[
\Delta p_x \sim \frac{\hbar}{\Delta x}
\]

Therefore, the confinement of the electron, otherwise free, along the x-axis will result in an increase in kinetic energy:

\[
E_{c,x} = \frac{(\Delta p_x)^2}{2m_e} \sim \frac{\hbar^2}{2m_e \sigma_x^2}
\]

where \( m_e \) is the effective mass of the electron. To get a feeling of the magnitude of this increase, we compare it to the thermal energy associated with a single degree of freedom:

\[
E_{c,x} \sim \frac{1}{2} k_B T
\]

where \( k_B \) is Boltzmann’s constant and \( T \) is the temperature. Simple algebra can show that, for the confinement energy to be significant, that is, comparable to the thermal
energy, there is a condition on the size of the confining length scale:

$$\sigma_x \sim \frac{\hbar}{\sqrt{m_e k_B T}} \quad (1.2)$$

In cadmium selenide (CdSe), $m_e = 0.13 m_0$, where $m_0$ is the mass of the free electron, yielding:

$$\sigma_x \leq 5.5 \times 10^{-9} m = 5.5 \text{nm}$$

at room temperature. This simple calculation shows that:

- If the confinement size decreases linearly, the confinement energy increases quadratically (equation 1.1);
- confinement effects become increasingly important for lower temperatures and effective masses (equation 1.2);
- since the effective mass typically lies in the range of $0.01 m_0 (\text{InSb}) \leq m \leq 1m_0 (\text{Si})$, the confinement size is also restricted to $1.7 \text{nm} \leq \sigma_x \leq 17 \text{nm}$, showing that confinement effects intrinsically reside at the nanoscale;

The increase in kinetic energy due to the confinement of a particle is known in the literature as the quantum confinement effect. The confinement energy goes to effectively increase the bandgap of the semiconductor $E_g \rightarrow E_g + E_c$. The immediate consequence of the quantum confinement effect is the possibility of tuning the material’s bandgap just by decreasing $\sigma_x$ and therefore increasing the confinement energy. So far we have considered the case of a particle confined along one direction of motion and free along the rest. We can identify semiconductor nanostructures according to their degree of confinement:

- **quantum wells** feature 1D confinement: $\sigma_x \leq \hbar / \sqrt{m_e k_B T}$;
- **quantum wires**, or nanowires, feature 2D confinement: $\sigma_x, \sigma_y \leq \hbar / \sqrt{m_e k_B T}$;
- **quantum dots**, feature 3D confinement: $\sigma_x, \sigma_y, \sigma_z \leq \hbar / \sqrt{m_e k_B T}$.

Confinement of charge carriers also affects the density of states $g(E) = dN/dE$, that is, the number of states available per unit energy. A simple calculation can show that $g(E, i) = E^{1/2(1-i)}$, where $i = [0, 1, 2]$ is the degree of quantum confinement. \[15\]

In the case of 3D confinement, the density of states becomes a collection of Dirac’s deltas, $g(E, 3) = \sum_j \delta(E - E_j)$ (see Figure 1.1 and section 1.1.10).

### 1.1.5 Discretization of electronic states

In the previous section we have followed a simple yet effective line of argument to disclose the quantum confinement effect and its importance at the nanoscale. We will now show that confining an electron also imposes a dramatic modification to the
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![Figure 1.1: Density of states of quantum confined objects.](image)

Dependence of the density of states $g(E)$ on the degree of confinement. From left to right: Bulk, quantum well, quantum wire, and quantum dot. Note how the increase in the degree of confinement transitions the density of states from continuous to discrete, while increasing the effective value of the bandgap.

Electronic states available. Consider now a slab of semiconductor crystal of thickness $\sigma_x \leq \hbar/\sqrt{m_e k_B T}$ and lateral dimensions $\sigma_y, \sigma_z \gg \hbar/\sqrt{m_e k_B T}$. Consequently, the electron is free along the y- and z-directions and confined along x: A quantum well. Let us consider the quantum well along the x-axis as an infinite potential well for the electron. We can therefore write:

$$V(x) = \begin{cases} 0 & \text{if } 0 \leq x \leq \sigma_x \\ +\infty, & \text{otherwise} \end{cases}$$

Since the particle is confined only in the x-direction and the well is infinitely deep, we can write the wave function for the electron as: \[ \Psi(x, y, z) = \phi(x)\psi(y, z) \] (1.3)

We can then treat separately the electron’s confined motion in the x-direction and the free motion in the y-z plane. The energy of a free particle can be written as

$$E_{\text{free}}(k) = \frac{\hbar^2 k^2}{2m_e}$$

and its motion is described by plane waves of the type

$$\psi(y, z) \propto e^{ik \cdot r}$$
where \( r \) and \( k \) span the 2D real and reciprocal spaces, respectively. What about the motion of the particle along the x-direction? Since the potential well is infinitely deep, we can reasonably assume that the probability for the particle to escape is negligible:

\[
\phi(x) = \begin{cases} 
    ?, & \text{if } 0 < x < \sigma_x \\
    0, & \text{otherwise}
\end{cases}
\]

where \( \phi(x) = 0 \) at the walls because of continuity arguments. Therefore the time-independent Schrödinger equation becomes:

\[
-k^2 \frac{d^2 \phi(x)}{dx^2} = E \phi(x)
\]

which can be easily rewritten as:

\[
\frac{d^2 \phi}{dx^2} + \kappa^2 \phi = 0 \quad \text{(1.4)}
\]

where \( \kappa = \sqrt{2m_e E/\hbar} \). Note that equation 1.4 in classical physics describes the harmonic oscillator, and a general solution can be written as

\[
\phi(x) = A \cos \kappa x + B \sin \kappa x
\]

where \( A \) and \( B \) are constants that can be determined by boundary conditions. Since we know that \( \phi(0) = 0 \), then \( B = 0 \) and \( \phi(x) = A \sin \kappa x \). We can also use the second boundary condition to obtain \( \phi(\sigma_x) = A \sin \kappa \sigma_x = 0 \). To have a non-trivial solution, \( A > 0 \), and we are left with a series of quantum numbers that satisfies the problem:

\[
\kappa_n = \frac{n \pi}{\sigma_x} \quad \text{(1.5)}
\]

where \( n \) is a positive integer. This imposes a limitation on the energy of the states of a particle confined in an infinitely deep well:

\[
E_n = \frac{\hbar^2 \kappa_n^2}{2m_e} = \frac{\hbar^2 \pi^2 n^2}{2m_e \sigma_x^2} \quad \text{(1.6)}
\]

For the lowest energy state, \( n = 1 \), we obtain \( E_1 = \hbar^2 \pi^2 / 2m_e \sigma_x^2 \), an expression extremely similar to the one calculated with the simple arguments followed in the previous section (equation 1.1). Finally, by imposing that the wave function must be normalized,

\[
\int_0^{\sigma_x} |\phi(x)|^2 dx = 1
\]

we obtain that \( A = \sqrt{2/\sigma_x} \). Therefore the motion of an electron in an infinitely deep well can be described by the envelope functions:

\[
\phi_n(x) = \sqrt{\frac{2}{\sigma_x}} \sin \left( \frac{n \pi}{\sigma_x} x \right) \quad \text{(1.7)}
\]
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The solution of the quantum problem of a particle confined in an infinitely deep well is not dissimilar from the solution of the classical problem of a string of length $\sigma_x$ and confined at its extrema. The excited states of the electron are standing waves increasing in frequency as a function of energy, and of alternating parity.

1.1.6 Electrons and holes

Bulk semiconductors are characterized by a fully occupied valence band and an empty conduction band at an energy offset $E_g$. When an electron is promoted to the conduction band, it leaves a positively charged hole behind. Until now we have considered only 1D confined electrons; however, holes are subject to quantum confinement as well. Typically, the effective mass of a hole is larger than that of an electron, with the notable exceptions of silicon and germanium. In CdSe for instance, the effective mass of the electron amounts to $m_e = 0.13m_0$ while for the hole $m_h = 0.45m_0$. A larger effective mass has influence on the confinement properties of the particle, as follows directly from equations 1.1, 1.2, and 1.6. Specifically, a larger effective mass:

- Decreases the confinement energy (equation 1.1);
- Makes it experimentally more challenging to observe confinement effects, as we need to work with smaller volumes (equation 1.2);
- Decreases the spacing between discrete energy levels $E_n$ (equation 1.6);

A cartoon illustrates these concepts for the effective masses of electron and hole of CdSe in Figure 1.2.

1.1.7 Absorption probability and selection rules

Let us now consider the probability of promoting one electron from the valence to the conduction band; let the excess energy we need be supplied by incident photons of energy $\hbar\omega$, propagating along the x-direction, the electric field polarized along the y-direction. In a quantum well, we are actually considering the transition between a quantum-confined state in the valence band identified by a quantum number $n$ and a state in the conduction band identified by a quantum number $n'$. According to Fermi’s golden rule, the corresponding transition probability can be written as:

$$W_{i \rightarrow f} = \frac{2\pi}{\hbar} |\langle i | - e \mathbf{r} \cdot \mathbf{E} | f \rangle|^2 g(\hbar\omega)$$

where $e$ is the electron’s charge and $\mathbf{r}$ is the position vector of the electron, $\mathbf{E}$ is the electric field vector, and $g$ is the joint density of states of electron and holes. The latter term simply means that there must be available states for the transition to take place at all, and the more available states the higher the transition probability. By following equation 1.3, the initial and final states can be written as:

$$\Psi_i \equiv |i\rangle = \frac{1}{\sqrt{V}} \phi_{hn}(x) \psi_{v}(y, z) e^{i k_y y} e^{i k_z z}$$
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Figure 1.2: Energy levels of a quantum confined 1D system and comparison to bulk properties. (Left) Discrete energy levels for electrons and holes confined in a 1D box of size $\sigma_x$. The position of the energy levels $E_n$ is generated from equation 1.6. The envelope functions $\phi_n(x)$ are also displayed (equation 1.7). For simplicity, this cartoon is limited to the four lowest energy states. (Right) Comparison with a bulk system. Note the lower bandgap. The continuous color shade indicates the density of states.

$$\Psi_f \equiv |f\rangle = \frac{1}{\sqrt{V}} \phi_{en'}(x)\psi_{c}(y, z)e^{iK_{y',z'}r_{y',z}}$$

where $V$ is a normalization constant. Note that the plane waves describe the free motion of electrons and holes only in the $y$-$z$ planes, as appropriate. We are therefore
left with matrix elements of the type

\[ M = \langle f | y | i \rangle = \int \Psi_f^* \Psi_i \, d^3r \]

which through separation of variables can be easily split into:

\[ M = M_{cv} M_{nn'} \]

where

\[ M_{cv} = \langle \psi_c | y | \psi_v \rangle \]

\[ M_{nn'} = \langle en | hn' \rangle \]

The term \( M_{cv} \) describes the probability of an interband electronic transition for the constituent material, for instance CdSe. Since these transitions are usually strongly allowed electric dipole transitions, we can assume \( M_{cv} > 0 \). Instead, the term \( M_{nn'} \) describes the probability of a transition between the valence and conduction states characterized by \( \Delta n = n' - n \). This term is a simple 1D integral:

\[ M_{nn'} = \frac{2}{\sigma_x} \int_{0}^{\sigma_x} \sin \left( \frac{n\pi x}{\sigma_x} \right) \sin \left( \frac{n'\pi x}{\sigma_x} \right) \, dx \]

yielding the selection rule

\[ \Delta n = 0 \quad (1.8) \]

Therefore, a transition between the confined states of a hole and an electron is only allowed if it takes place between states of equal quantum number \( n \). This selection rule now allows us to consider the light absorption properties of a quantum confined system. Figure 1.2 shows us that the energy needed to excite an allowed interband transition is

\[ \hbar \omega = E_g + E_{en} + E_{hn} \]

which we can rewrite by using equations 1.6 and 1.8 as:

\[ \hbar \omega = E_g + \frac{\hbar^2 \pi^2 n^2}{2\sigma_x^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) = E_g + \frac{\hbar^2 \pi^2 n^2}{2m^* \sigma_x^2} \quad (1.9) \]

where \( m^* = m_e m_h / (m_e + m_h) \) is the reduced effective mass of electron and hole.

### 1.1.8 Excitons

Up to now we have treated the behavior of electrons and holes separately. This is only acceptable if their Coulombic interaction is negligible compared to the confinement energy, that is, when the confinement size is smaller than the size of a bound electron-hole pair, also known as exciton. The Bohr model can give a rough estimate
of the size of an exciton, provided we correct for the reduced effective mass of the electron-hole pair $m^*$ and the dielectric constant of the medium $\varepsilon$:

$$a_X = \frac{4\pi\varepsilon_0\varepsilon\hbar^2}{e^2m^*}$$

(1.10)

For CdSe, this gives $a_X = 5.4\text{nm}$ for the size of an exciton, or the exciton Bohr radius. We can therefore distinguish the following confinement regimes:

- **strong confinement**, when $\sigma_x < a_X$ and the confinement energy dominates over the Coulombic component;
- **weak confinement**, when $\sigma_x > a_X$, viceversa.

Interestingly, the estimate we made in equation 1.2 about the minimum size below which we should expect confinement effects, agrees very well with the exciton Bohr radius.

### 1.1.9 Light emission

An electron excited to the conduction band and a hole in the valence band can recombine through the emission of a photon. Quantum confinement increases the probability of this process by increasing the overlap of electron and hole wave functions in the quantum confined object. Simply, the two charge carriers have nowhere else to go. Suppose to have an electron and a hole excited in the $n$-th state, with $n > 1$. The charge carriers can relax, or cool down, to the lowest energy state in the conduction and valence bands, corresponding to $n = 1$, through the emission of phonons, vibrations of the atomic lattice. Then, the electron and hole can recombine radiatively through the emission of a photon of energy

$$\hbar\omega = E_g + E_{e1} + E_{h1} = E_g + \frac{\hbar^2\pi^2}{2m^*\sigma_x^2}$$

We can therefore unveil another advantage of quantum confinement: by changing the confining dimension $\sigma_x$ we can tune not only the effective energy gap, but also the emission energy. These concepts are illustrated in a cartoon in Figure 1.3.

### 1.1.10 Quantum dots

So far we have considered the case of a quantum well, where quantum confinement is only significant along one direction of motion of electron and holes, while motion is not constricted along the other two directions. Though quantum wells represent the simplest example of quantum confined objects and are of interest to this thesis, we will now consider the case of 3D quantum confinement. Nanostructures where the charge carriers are confined along all three directions of motion are usually described as quantum dots. In the case of a 3D and infinitely deep potential well, we can treat the
Figure 1.3: Intraband relaxation of electrons and holes and radiative recombination. Electrons and holes can relax to the first excited state, \( n = 1 \), through the emission of phonons of energy \( \hbar \omega_{ph} \) equal to the energy spacing. After full relaxation, electrons and holes can recombine radiatively through the emission of a photon of energy \( \hbar \omega = E_g + E_{e1} - E_{h1} \).

Problem separately along each direction of motion and the confinement energy adds up to:

\[
E_{n_x n_y n_z} = E_{n_x} + E_{n_y} + E_{n_z} = \frac{\hbar^2 \pi^2}{2m_e} \left( \frac{n_x^2}{\sigma_x^2} + \frac{n_y^2}{\sigma_y^2} + \frac{n_z^2}{\sigma_z^2} \right)
\]

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The confinement energy increases for each additional direction of motion along which the electron is confined. In the case of a cubic box \( \sigma_x = \sigma_y = \sigma_z = \sigma \):

\[
E_c = \frac{\hbar^2 \pi^2}{2m_e \sigma^2} (n_x^2 + n_y^2 + n_z^2)
\]

An identical result is valid for the hole with the substitution \( m_e \rightarrow m_h \). A few considerations are due:

- Like in quantum wells, also in quantum dots the bandgap \( E_g \) of the material increases by an amount \( 3\hbar^2 \pi^2 / 2m^* \sigma^2 \) which is inversely proportional to the square of the size of the quantum dot \( \sigma \). Consequently, the energy of emitted photons through radiative recombination of an electron-hole pair will also be tunable through the same mechanism;

- unlike in quantum wells, the motion of charge carriers is confined along all directions, resulting in zero degrees of freedom. The energy spectrum of a quantum dot is therefore entirely determined by the vector \( \mathbf{n} = (n_x, n_y, n_z) \) and therefore, discrete. For this reason, quantum dots are sometimes referred to as artificial atoms;

- the discrete nature of the density of states has a very interesting advantage on charge carrier cooling. The cooling of an electron from the \( n \)-th excited state to the one below must result in the emission of a phonon with a specific energy \( E_n - E_{n-1} \). It is therefore possible that this requirement may slow down charge carrier cooling, allowing the extraction of extra energy that is otherwise quickly lost as heat. This effect is known in the literature as phonon bottleneck; \[17\]

- the character of confined electronic states increases the probability of radiative recombination even more through the increase in wave functions’ overlap, making quantum dots very promising photon emitters; \[18\]

- quantum dots are usually rather spherical-like than cubic. The solution of the time-independent Schrödinger equation for the case of a sphere can conceptually follow the same steps as in section 1.1.5 but the symmetry of the problem suggests a change of coordinate system from rectangular to spherical; rather than the product of three sinusoidals, the envelope functions \( \phi(r) \) are best described by a product of spherical harmonics and a radial Bessel functions. \[5\] Therefore, the mathematical problem and therefore its solutions resemble closely that of the hydrogen atom: The energy levels for the confined electron can be written as:

\[
E_{nl} = \frac{2\hbar^2 \chi_{nl}^2}{m_e \sigma^2}
\]  

(1.11)
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Here $\chi_{nl}$ are the roots of the Bessel function and depend on the principal $n$ and azimuthal $l$ quantum numbers. It is therefore not surprising that the symmetry of the wave functions of an electron confined in a spherical quantum dot resemble the orbitals of the hydrogen atom. For this reason, also in quantum dots the electronic states are generally described by the value of the quantum number $n$ and a letter describing the symmetry (S, P, D). One may speak of a state $1S_e$, for instance.

1.1.11 Colloidal quantum dots

Quantum dots were first discovered and studied independently by Brus and Ekinov in the early 80’s. [19, 20] After three decades spent improving fabrication methods and our physical understanding of these systems, quantum dots-based applications landed on the market, the most successful example probably being the quantum dot television by Samsung, QLED. [21]

Although at the beginning quantum dots were produced as a dispersion in a glassy matrix, today they are mostly synthesized as a colloidal dispersion. While the core properties remain essentially unaffected, the surface acquires a fundamentally important role in mediating the interaction between the core and surrounding solvent molecules, neighboring quantum dots, and contacts. If we consider a sphere, the surface per unit volume increases with $1/\sigma$ for decreasing diameter; by using this simple argument on a CdSe quantum dot of diameter $\sigma = 5.4nm$, we can estimate that $\sim 53\%$ of the quantum dot volume is taken up by atoms within a lattice constant from the surface. In solid-state physics, the surface of a crystal is often regarded as a very large defect, since by definition it represents an interruption of the lattice. The same is true with quantum dots: undercoordinated surface atoms can act as recombination centers for electrons and holes, introducing localized states deep within the bandgap that act as traps. To counter this effect, a set of ligand molecules can be introduced with the following functions:

- Passivating surface traps;
- providing the insulating barrier that allows for quantum confinement;
- setting the distance between neighboring particles;
- allowing dispersibility in a solvent;
- mediating the interaction between neighboring quantum dots.

The role of the ligands in mediating the interaction between neighboring quantum dots is especially important in the assembly properties of these systems. The assembly of quantum dots is fundamentally important to the development of novel artificial solids. In the next section we will explore further these concepts.
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1.1.12 Artificial solids based on quantum dots

The optoelectronic properties of quantum dots intrinsically descend from confining charge carriers to small volumes comparable in size to the exciton Bohr radius \( a_X \). Similarly to atoms, quantum dots can assemble into dense phases such as amorphous and crystalline solids. As the interdot distance decreases, the overlap between neighboring quantum dot wave functions can become significant, and the unperturbed electronic states can interact to form hybridized molecular states or orbitals. When forming a solid composed of a large number of quantum dots, the discrete electronic states can hybridize to form electronic bands; to distinguish these bands from those deriving from the electronic coupling of atoms, we will address them as *minibands*. [22]

Minibands are of fundamental importance to the development of novel optoelectronic devices based on quantum dots: Through minibands, the wave function of an electron excited within a single quantum dot can spread throughout the whole quantum dot solid, allowing for faster conduction of charges. [23–26] A cartoon illustrates these concepts in Figure 1.4.

However, some of the characteristics of quantum dots make miniband formation harder to achieve and exploit with respect to the atomic case: [27-28]

- **Energetic and structural disorder**: Even though modern fabrication techniques have achieved remarkably high and consistent sample uniformity, size polydispersity lies in the way of producing strongly coupled quantum dot solids. The distribution of quantum dot diameters is usually described in terms of the polydispersity as \( \Delta \sigma/\sigma \), the width of the diameter distribution divided by the average diameter. The lowest polydispersity values achieved today lie in the range of \( \Delta \sigma/\sigma \approx 3\% \). [29] From equation 1.11, we know that a linear increase in diameter will result in a quadratic negative shift in energy therefore leading to energetic disorder. For CdSe, we can easily compute that a polydispersity of 6% introduces a maximum energy barrier of \( E_a \approx k_B T \) for the first electronic excited state across the ensemble. If two states are separated in energy by \( E_a > k_B T \), then charges need to hop from one dot to another and the probability of this process quickly decreases with \( E_a \) and interparticle distance \( d \) according to \( p_{\text{hop}} \propto e^{-\beta d-E_a/k_B T} \), where \( \beta = 2\sqrt{2m_e V_B} / \hbar \) is the wave function attenuation through a barrier of width \( d \) and height \( V_B \). [27-30]

The expression for \( p_{\text{hop}} \) pictures a road map to improving electronic coupling in quantum dot solids. Employing shorter ligands decreases \( d \), but may also change \( \beta \). For insulating alkane ligands \( \beta \sim 11 nm^{-1} \), [31] while employing phenyl ligands can halve this value. [30] Using organic conjugated ligands or inorganic solders should allow for even lower \( \beta \) values, therefore improving electronic coupling. [32] Specifically, the use of molecular solders should ideally bring \( V_B \) to zero because of the composition-match.
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Figure 1.4: Electronic coupling of individual quantum dot states into minibands. At large interdot distances, quantum dot states cannot couple efficiently because of the reduced overlap of their wave functions. For shorter interdot distances, it is predicted that individual quantum dots states can couple to form bands.

- **Electronic traps**: The access to a miniband does not imply that the carriers will be able to live long enough to increase macroscopic conductivity. If a secondary recombination channel is available, such as localized states deep within the bandgap, charges may be temporarily or permanently removed from the conductive channel. Surface defects on the surface of QDs can provide such recombination centers, that therefore need to be removed through efficient surface passivation or doping. [25]
• **Colloidal nature:** Colloidal quantum dots need to be assembled in a close-packed solid with short surface-to-surface distances to experience strong coupling effects. To do so, the pairwise interactions that control the assembly must be properly exploited. In the next section, we will review these interactions.

Despite the mentioned practical complications, the prospect of building novel artificial solids is attractive. The emerging electronic properties of the artificial solid built from the bottom-up with colloidal quantum dots will be defined by the choice of quantum dot material, size, superlattice constant, and surface chemistry. It is possible to imagine that specific combinations of quantum dots may yield materials with novel properties with respect to ordinary atomic solids.

1.2 **Pairwise interactions in colloidal science**

Quantum dots in solution form a colloidal dispersion, in which the particles can interact through a number of forces. The most basic colloidal interaction that describes the stability or aggregation of colloidal dispersions is given by the DLVO theory.

### 1.2.1 DLVO theory

The DLVO theory is named after Boris Derjaguin and Lev Landau, Evert Verwey and Theodor Overbeek, who independently developed it in the 40’s. The DLVO theory can quantitatively address the stability of colloidal dispersions by considering the effective potential experienced by the dispersed particles as a superposition of short-ranged attractive and long-ranged repulsive interactions. Specifically, the attractive interaction is based on van der Waals forces, while the repulsive component describes screened electrostatics. Their superposition yields a potential of the type shown in Figure 1.5. Depending on the relative magnitude of the attractive and repulsive components, the shape of the DLVO potential can vary dramatically. The dominance of the attractive component will yield an attractive potential with a single, deep, primary minimum at contact; conversely, a strong interparticle repulsion will yield a repulsive potential. Instead, carefully balanced interactions can yield more complex scenarios such as the one shown in the figure, showing a two minima separated by an energy barrier, \( E_b \). The probability for the particle to cross the barrier decreases exponentially with \( E_b \): \( p \sim e^{-E_b/k_B T} \). In the following sections we will review the fundamentals of these interactions.
Chapter 1. General Introduction

Figure 1.5: Schematic of typical DLVO pair potentials. The superposition of the repulsive screened electrostatic interaction (red) with the attractive van der Waals component (blue) yields an effective potentials of the type shown here (green). The DLVO potential can show a deep primary minimum, of depth $\gg k_B T$ descriptive of the dominance of the van der Waals component at short length scales, and a shallow secondary minimum, usually of depth $\sim k_B T$. A potential barrier separates the two minima.

1.2.2 Van der Waals interactions

Let us consider the Bohr model once again, where the electron circles around a proton in fixed orbits, the smallest of which has a radius $a_0$ known as the Bohr radius:

$$a_0 = \frac{4\pi \varepsilon_0 h^2}{m_0 e^2}$$

(1.12)

If we define the dipole moment as $\delta = a_0 e \mathbf{r}$ then it will be clear that the average in time of the dipole moment $\langle \delta \rangle = 0$. However, at any given time $t$, $\delta(t) \neq 0$. The electric field of this dipole can polarize a second neutral atom nearby, giving rise to an attractive interaction between a dipole and an induced dipole. These interactions are well-known in electrostatics and the energy of this interaction is given by:

$$U_L = -\frac{\delta^2 \alpha_0}{(4\pi \varepsilon_0)^2 d^6} = -\frac{(a_0 e)^2 \alpha_0}{(4\pi \varepsilon_0)^2 d^6}$$

where $\alpha_0$ is the polarizability of the second atom and $d$ is the interparticle distance. This interaction energy is known as the London energy, and is one of the three con-
1.2. Pairwise interactions in colloidal science

Contributions to the van der Waals interaction. The other two components involve the electrostatic interaction between one permanent dipole and one polarizable atom or molecule, known as the Debye energy, and between two permanent freely rotating dipoles, Keesom energy. Since all of these interactions involve two dipoles or two polarizable atoms or molecules through London’s interaction, they all share the same $d^{-6}$ behavior. By considering the electrostatic interaction as instantaneous, and therefore by neglecting any retardation effects due to information travel time from dipole to polarizable atom or molecule, Hugo Christiaan Hamaker in 1937 derived the general interaction energy for two spheres of radii $r_1$ and $r_2$ separated by a distance $d$:

$$U_{vdW}(d) = -\frac{A}{6} \times \frac{2r_1 r_2}{(2r_1 + 2r_2 + d)d} + \frac{2r_1 r_2}{(r_1 + d)(2r_2 + d)} + \ln \frac{(2r_1 + 2r_2 + d)d}{(r_1 + d)(2r_2 + d)}$$  (1.13)

where $A$ is known as the Hamaker constant, typically in the ballpark of $10^{-19}\text{J}$.

In case the of $r_1 = r_2 = \sigma/2$ equation (1.13) simplifies to:

$$U_{vdW}(d) = -\frac{A}{12} \left[ \frac{\sigma^2}{(2\sigma + d)d} + \frac{\sigma^2}{(\sigma + d)^2} + 2\ln \frac{(2\sigma + d)d}{(\sigma + d)^2} \right]$$  (1.14)

This interaction is surprisingly strong and short-ranged. By taking $A = 10^{-19}\text{J}$ and $\sigma = 5.4\text{nm}$, $U_{vdw} = -0.3k_B T$ at $d = 2\text{nm}$, but quickly increases in magnitude to reach $-18k_B T$ at $d = 0.2\text{nm}$. The actual calculation of the Hamaker constant in the case of two media 1 and 2 interacting through a third medium $m$ has been performed by Lifshitz, to yield the following expression:

$$A \approx \frac{3}{4} k_B T \frac{\epsilon_1 - \epsilon_m \epsilon_2 - \epsilon_m}{\epsilon_1 + \epsilon_m \epsilon_2 + \epsilon_m} + \frac{3}{2} \hbar \int_{k_B T/h}^{+\infty} \frac{\epsilon_1(i\nu) - \epsilon_m(i\nu) \epsilon_2(i\nu) - \epsilon_m(i\nu)}{\epsilon_1(i\nu) + \epsilon_m(i\nu) \epsilon_2(i\nu) + \epsilon_m(i\nu)} d\nu$$  (1.15)

where $\epsilon_1, \epsilon_2, \epsilon_m$ are the static dielectric constants of the three media, and $\epsilon(i\nu)$ are the values of the dielectric response at imaginary frequencies. In the symmetric case, $\epsilon_1 = \epsilon_2 = \epsilon_p$, this expression reduces to:

$$A \approx \frac{3}{4} k_B T \left( \frac{\epsilon_p - \epsilon_m}{\epsilon_p + \epsilon_m} \right)^2 + \frac{3}{2} \hbar \int_{k_B T/h}^{+\infty} \left( \frac{\epsilon_p(i\nu) - \epsilon_m(i\nu)}{\epsilon_p(i\nu) + \epsilon_m(i\nu)} \right)^2 d\nu$$  (1.15)

The first term, the zero frequency component, describes the Debye and Keesom interactions, while the second term describes the London contribution. Solving this integral depends critically on the type of medium we are considering. Since usually the medium is a dielectric, we will briefly consider the cases of dielectric or metallic particles interacting in a dielectric medium.
• for dielectric particles we can write \( \epsilon_d(i\nu) = 1 + (n^2 - 1)/(1 + (\nu/\nu_{e,d})^2) \), where \( n \) is the refractive index of the dielectric and \( \nu_{e,d} \) is the main electronic absorption frequency in the UV, typically around \( 10^{15}\text{s}^{-1} \). For instance, the main alkanes \( C_nH_{n+2}, 5 \leq n \leq 16 \) and water all have \( \nu_{e,d} = 3 \times 10^{15}\text{s}^{-1}. \) [34] In this case, equation [1.15] yields the following expression for the Hamaker constant:

\[
A \approx \frac{3}{4}k_B T \left( \frac{\epsilon_p - \epsilon_d}{\epsilon_p + \epsilon_d} \right)^2 + \frac{3h\nu_{e,d} (n_p^2 - n_d^2)^2}{16\sqrt{2} (n_p^2 + n_d^2)^{3/2}}
\]

• for metallic particles instead, \( \epsilon_{metal}(i\nu) = 1 + (\nu_{e,metal}/\nu)^2 \) where \( \nu_{e,metal} = \sqrt{ne^2/e_0 m_e/2\pi} \) is the plasma frequency and \( n \) the electron density. Notable examples of \( \nu_{e,metal} \) are: \( 2.7 \times 10^{15}\text{s}^{-1} \) for Indium, \( 3.7 \times 10^{15}\text{s}^{-1} \) for Aluminum, \( 4.6 \times 10^{15}\text{s}^{-1} \) for Copper, and \( 6.2 \times 10^{15}\text{s}^{-1} \) for Gold. [37] In the case of metallic particles the solution of equation [1.15] yields:

\[
A \approx \frac{3}{4}k_B T + \frac{3h\nu_{e,metal}}{16\sqrt{2}} \frac{(\sqrt{2} + c)^3 - (\sqrt{2} + 2c)(n_d^2 - 1) + (n_d^2 - 1)^2/c}{(\sqrt{2} + c)^2 + n_d^2 - 1)^{3/2}}
\]

where \( c \equiv \nu_{e,metal}/\nu_{e,d}. \)

Since the value of the Hamaker constant for CdSe is important to this thesis, we report the values calculated for quantum dots interacting through three notable media: vacuum \( A_{CdSe,vac,CdSe} = 1.6 \times 10^{-19}J \approx 39k_B T \), hexane \( A_{CdSe,C_6H_{14},CdSe} = 0.5 \times 10^{-19}J \approx 12k_B T \), and chloroform \( A_{CdSe,CHCl_3,CdSe} = 0.4 \times 10^{-19}J \approx 9k_B T. \) [39]

Typically, van der Waals forces lead to a strongly attractive minimum in the pair potential of colloidal particles that causes particles to quickly assemble irreversibly and fall out of solution. To ensure the dispersibility and colloidal stability of colloidal particles, it is therefore necessary to introduce a repulsive interaction to contrast the van der Waals attraction and yield colloidal stability particles. Electrostatic and steric interactions can help prevent irreversible aggregation in, respectively, polar and nonpolar solvents.

### 1.2.3 Electrostatic interactions

The surface of a particle can become charged in one of the following ways:

- **dissociation of surface groups.** Ligands bound to a QD can feature a functional group that can lose or gain \( z \) protons upon exposure to a solvent in basic or acidic conditions. The ligand becomes therefore charged with a charge \( ze \), and the sum of all charges from all ligands amounts to the surface charge of the quantum dot: \( \pi e z \Gamma / \sigma^2 \).

- **adsorption or binding of ions from solution;**
1.2. Pairwise interactions in colloidal science

Figure 1.6: Schematic describing charged surfaces in a polar solvent. (Left) Two charged surfaces in a polar solvent with dielectric constant $\epsilon$ and charge density $ze\Gamma$, separated by a distance $d$. A certain concentration of dissociated counterions are present between the two surfaces. (Right) Counterion density profile $\rho(x)$ and electrostatic potential $V(x)$ are schematically shown, together with their values at the surface, $\rho_S$ and $V_S$. Figure adapted from the literature. [34]

- charge exchange. This is the case when two surfaces are close to each other and $ze$ charges can hop from a neighboring surface resulting in oppositely charges surfaces.

Let us consider the first case. The counterions are either transiently bound to the surface within the so-called Stern layer, or form a cloud of rapidly diffusing ions surrounding the surface in the so-called electric double-layer. The counterions are attracted to the surface via electrostatics but this contribution is balanced by the gain in free energy due to the increase in configurational entropy in the dissolved state. The chemical potential of any ion bearing a charge $ze$ can be written as

$$
\mu(x) = zeV(x) + k_BT \ln \rho(x)
$$

where $V$ is the electrostatic potential and $\rho$ is the charge density (see Figure 1.6). If two surfaces are separated by a certain distance, we can set $V(0) = 0$ at the midplane $x = 0$, where for simplicity we are considering only the 1D case. Since at equilibrium the chemical potential must be equal for all points in space, we can write that the chemical potential at the midplane must equal the chemical potential at any point $x$:

$$
\mu(x) = \mu(0)
$$

which yields

$$
zeV(x) + k_BT \ln \rho(x) = k_BT \rho(0)
$$
solving which we obtain that:

$$\rho(x) = \rho(0)e^{-zeV(x)/k_BT} \quad (1.16)$$

which is known as the \textit{Nernst equation}. This equation states that the charge density due to the counterions in solution corresponds to the Boltzmann distribution. We can use this result with the \textit{Poisson equation}:

$$\frac{d^2V}{dx^2} = -\frac{ze \rho(0)}{\epsilon \epsilon_0}e^{-zeV/k_BT} \quad (1.17)$$

which is known as the \textit{Poisson-Boltzmann equation}. By solving this equation we can obtain the profiles of the electrostatic potential $V$, charge density $\rho$ and electric field $-dV/dx$ between the two surfaces. By differentiating equation 1.16 and using 1.17 and integrating, we can obtain the charge density at the surface:

$$\rho_S = \rho(0) + \frac{z^2 e^2 \Gamma^2}{2 \epsilon \epsilon_0 k_B T}$$

This expression shows that even when the two surfaces are very far apart so that $\rho(0) \rightarrow 0$, there is always a residual charge density at the surface that represents the diffuse ion double layer. The ion concentration of this double layer is proportional to the square of the charge density $ze\Gamma$, and inversely proportional to $k_BT$ as expected since the ions can escape if they are given enough thermal energy.

By solving the equation 1.17 in the case of parallel, flat, charged surfaces in the presence of an ion concentration $\rho$, and applying the Derjaguin approximation (see appendix to this chapter), we obtain the interaction free energy for spheres or diameter $\sigma$:

$$U_{ES}(d) = \frac{\sigma}{4} Z e^{-d/\lambda_D} \quad (1.18)$$

where $Z = 64\pi \epsilon \epsilon_0 (k_B T/e)^2 \tanh^2 (zeV_S/4k_BT)$, $V_S$ is the potential at the surface, and

$$\lambda_D = \sqrt{\frac{\epsilon \epsilon_0 k_B T}{2 N_A e^2 I}}$$

is the \textit{Debye screening length}, and $I$ the ionic strength. The Debye screening length determines the length scale of the screened electrostatic potential: For $V_S < 25 mV$ we can write $V(x) = V_S e^{-x/\lambda_D}$ and therefore $\lambda_D$ represents the distance at which the potential has dropped by a factor $1/e$ from the surface value. In these conditions of low surface potentials, equation 1.18 can be simplified to yield:

$$U_{ES}(d) = \frac{\pi \sigma z^2 e^2 \Gamma^2 \lambda^2}{\epsilon \epsilon_0} e^{-d/\lambda_D} \quad (1.19)$$
1.2. Pairwise interactions in colloidal science

where we have made use of the approximation to the Grahame equation for low potentials, \( V_S = z e \Gamma \lambda_D / \varepsilon \varepsilon_0 \). Therefore we can observe that \( \lambda_D \) controls not only the length scale of the interaction, but also the magnitude, together with the surface charge density. A very effective way to act on the electrostatic interaction is to screen the potential by decreasing the value of Debye screening length \( \lambda_D \): This is easily done by increasing the concentration of ions in solution, therefore increasing the ionic strength \( I = 1/2 \sum_{i=1}^{n} \rho_i z_i^2 \) summed on all anions and cations of valency \( z_i \) and concentration \( \rho_i \) present in solution. For monovalent ions we obtain \( I = \rho \), and in case of water at room temperature the expression for \( \lambda_D \) simplifies to

\[
\lambda_D (\text{nm}) = \frac{0.304}{\sqrt{I(\text{moles/L})}}
\]

1.2.4 Steric repulsion

Bulky ligands grafted on the surface of quantum dots can act as entropic spacers, efficiently counteracting van der Waals forces, and yielding a colloidal stable dispersion. These ligands are essentially surfactant molecules, and can be usually represented as long, more or less flexible, nonpolar hydrocarbon chains bound to a polar head group. The nonpolar chain essentially functions as a spacer, keeping quantum dot surfaces far apart to prevent aggregation via van der Waals, while the head group binds to one or multiple sites on the surface of the quantum dot. The colloidal nature of a quantum dot is largely defined by the nature of the ligands bound to the surface. When the bound ligand molecules are in contact with a good solvent, then the solvent-ligand interaction is stronger than the ligand-ligand interaction, ligand chains repel one another and dangle out in solution where they are thermally mobile: this results in a colloidal stable dispersion. However, if the ligands are in contact with a bad solvent, meaning that the ligand-ligand interaction is stronger than the ligand-solvent interaction, than the ligand chains will become attractive and collapse on each other. To minimize the surface area exposed to the bad solvent, quantum dots will coagulate and flocculate, resulting in an aggregated colloid. As a rule of thumb, if a certain solvent is a good solvent for a specific ligand then it will be a good dispersing medium for a quantum dot dispersion passivated by the same ligand, and viceversa.

Let us imagine then two quantum dots diffusing in a good solvent, randomly colliding in solution. The dangling state of ligand chains is entropically favored over the collapsed state, that is to say it represents a macrostate of the system that can be realized by a much larger number of microstates. When the two surfaces approach, the confinement of the dangling chains will therefore restrict the number of available microstates and result in a fundamentally entropic repulsive force driven by the increase in osmotic pressure. This force is known as steric or overlap repulsion. We can quantify the corresponding interaction energy from the surface density of ligands
bound to the surface, which is fundamentally limited by the number of binding sites
and by the steric hindrance of the ligands. For the case of oleate ligands bound to
CdSe quantum dots, typical surface coverages are $1.5 \text{nm}^{-2} \leq \Gamma \leq 3.5 \text{nm}^{-2}$. [40]
meaning the average distance between binding sites $s = \sqrt{1/\Gamma}$ lies in the range of
$0.5 \text{nm} \leq s \leq 0.8 \text{nm}$. [34] We are therefore in the regime of high grafting density,
since $s > R_g = 0.26 \text{nm}$ where $R_g$ is the gyration radius of the ligand. [41] Intui-
tively, we can expect the ligand chains to dangle out in solution to form a brush of
average thickness $h_0$ that defines the length scale of steric repulsion. By following
self-consistent field theory, [42] and using the Derjaguin approximation (see appendix
to this chapter), for $h_0 \ll \sigma$, [43] we obtain the following expression:

$$U_{\text{steric}}(d) = \frac{\pi^3 \Gamma \sigma h_0^3 k_B T}{240 N b^2} \times$$
$$\left[ -45 - 30 \ln \frac{d}{2h_0} + 54 \frac{d}{2h_0} - 10 \left( \frac{d}{2h_0} \right)^3 + \left( \frac{d}{2h_0} \right)^6 \right] (1.20)$$

where we treat the ligand as a polymer composed of $N$ monomers of length $b$.

The steric interaction can efficiently stabilize colloidal nano- and microparticles
against aggregation via van der Waals forces. However, the nonpolar ligand chains
require the use of a nonpolar solvent. Instead, to guarantee a well dispersed colloid in
polar solvents, we must resort to electrostatic repulsion.

### 1.2.5 Depletion interaction

We have seen that entropy can play a key role in determining the magnitude of an
interaction. This is also the case for attractive depletion forces, when large molecules
are not surface-bound but rather free in solution. Imagine to have two spheres of di-
ameter $\sigma$ dispersed in a solvent, together with smaller spheres of diameter $\sigma_{\text{dep}} < \sigma$. Suppose that the larger spheres collide due to Brownian motion in solution: When
their interparticle distance drops below $d < \sigma_{\text{dep}}$, the smaller spheres will be geo-
metrically excluded from the overlap region which will become depleted of smaller
spheres (see Figure 1.7). At the same time, the total volume available to the smaller
spheres will increase by $\Delta V$, resulting in a decrease in the free energy of the system

$$U = -k_B T \ln Q = -N k_B T \ln (V_0 + \Delta V) \approx -N k_B T \left( \ln V_0 + \frac{\Delta V}{V_0} \right)$$

where $Q$ is the total partition function of the system which in conditions of high dilu-
tion can be approximated by $Q \approx V^N$, where $N$ is the number of depletant particles.
The free energy of the interaction is then given by

$$\Delta U(d) = U(d) - U(+\infty) = -N k_B T \frac{\Delta V}{V_0}$$

This simple consideration shows the main features of this interaction: [33]
1.2. Pairwise interactions in colloidal science

Figure 1.7: Schematic of depletion interaction. Nonadsorbing depletant objects of size $\sigma_{\text{dep}}$, blue spheres, produce an attraction between larger objects of size $\sigma$, maroon spheres, with a range of interaction comparable to $\sigma_{\text{dep}}$. The green box highlights the depleted region.

- the depletion interaction is attractive;
- the magnitude of the interaction is directly proportional to the concentration of depletants, $\rho = N/V_0$, and to the osmotic pressure $P = \rho k_B T$;
- the length scale of the interaction can be intuitively linked to the size $\sigma_{\text{dep}}$ of the depletants, for if $d \geq \sigma_{\text{dep}}$ there is no depletion at all.

Once again we can consider the case of $\sigma_{\text{dep}} \ll \sigma$ and apply the Derjaguin approximation (see appendix to this chapter), to calculate the free energy of the interaction in the case of spheres. This yields:

$$U_{\text{dep}}(d) = -\frac{1}{4} \pi \sigma R_g^2 P \left(1 - \frac{d}{R_g}\right)^2$$  \hspace{1cm} (1.21)

which confirms our expectations that the magnitude of the interaction should depend on the osmotic pressure and that the length scale should be related to the size of the depletant. It also becomes clear that the best way to increase the magnitude of this
interaction is to increase the concentration of depletants. The nature of the depletants can range from dissolved polymer chains, to micelles, to hard spheres.

### 1.2.6 Critical Casimir interaction

In 1948, Hendrik Casimir predicted that two parallel and conductive plates separated by a distance $d$ and immersed in the electromagnetic quantum vacuum should experience an attractive force per unit area: \[ F_C \] \[ \frac{S}{S} = -\frac{\hbar c \pi^2}{240d^4} \]

Thirty years later, Fisher and de Gennes predicted that a similar effect should arise in the perfectly classical system of two surfaces immersed in a binary fluid mixture close to its critical point: \[ F_{CC} \] Under these conditions, solvent density fluctuations of average size $\xi$, the correlation length, arise and, when confined between the two surfaces, induce an attractive force. This effect becomes particularly significant near the critical point of the solvent, where $\xi$ becomes comparable to the distance between the surfaces $d$. Close to the critical point, the solvent correlation length obeys the universal relation:

\[
\xi(T) = \xi_0 \left| \frac{T - T_c}{T_c} \right|^{-0.63}
\]  

where $T_c$ is the critical temperature of the solvent. In their original paper, Fisher and de Gennes proposed that the free energy of the interaction should behave like:

\[
U_{CC} \approx -\frac{k_B T}{\xi^2} e^{-d/\xi}
\]  

To derive the free energy of the interaction in the case of spheres of diameter $\sigma$ we can use the Derjaguin approximation, valid for $\xi \ll \sigma$ (see appendix to this chapter), to yield:

\[
U_{CC} \approx -\frac{\pi \sigma k_B T}{\xi} e^{-d/\xi}
\]

We can therefore infer that the correlation length of the fluctuations $\xi$ controls both the magnitude and the length scale of the interaction.

The critical Casimir interaction can seem somewhat more obscure compared to well-known electrostatics and sterics; however, being a solvent-mediated interaction, it has attracted considerable attention in recent years. The reason for this is that the critical Casimir interaction can be entirely controlled by simply changing the temperature of the near-critical solvent, leaving other interactions unaffected. The power-law dependence of $\xi$ on $\Delta T$ implies continuous changes of the critical Casimir potential with temperature that can finely tuned in situ, providing a direct physical knob to control the interaction.
1.3. Synergy of this thesis

1.2.7 Summary

To conclude this section, we summarize the most important colloidal interactions in the table below. They will find applications in the rest of this thesis.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Validity</th>
<th>Interaction free energy</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>van der Waals</td>
<td>Non retarded</td>
<td>$-\frac{A}{12} \left[ \frac{\sigma^6}{(2\sigma + d)^6} + \frac{\sigma^6}{(\sigma + d)^6} + 2 \ln \frac{(2\sigma + d)\sigma}{(\sigma + d)^2} \right]$</td>
<td>1.14</td>
</tr>
<tr>
<td>Sterics</td>
<td>$\max(h_0, d) \ll \sigma$</td>
<td>$\frac{\pi^2 k_B^2}{2 \sigma h_0^2} \left[ -45 - 30 \ln \frac{h_0}{d} + 54 \frac{d}{h_0} - 10 \left( \frac{d}{h_0} \right)^3 + \left( \frac{d}{h_0} \right)^6 \right]$</td>
<td>1.20</td>
</tr>
<tr>
<td>Electrostatics</td>
<td>$\max(\lambda_D, d) \ll \sigma$</td>
<td>$16\pi \varepsilon \varepsilon_0 \frac{k_B T}{\epsilon} \left( \frac{4eV}{4k_B T} \right)^2 e^{-d/\lambda_D}$</td>
<td>1.18</td>
</tr>
<tr>
<td>Depletion</td>
<td>$\max(\sigma_{dep}, d) \ll \sigma$</td>
<td>$-\frac{1}{4} \frac{k_B}{\epsilon} R_g^2 \mu k_B T \left( 1 - \frac{d}{R_g} \right)^2$</td>
<td>1.21</td>
</tr>
<tr>
<td>Critical Casimir</td>
<td>$\max(\xi, d) \ll \sigma$</td>
<td>$-\frac{\pi k_B T}{\xi} e^{-d/\xi}$</td>
<td>1.24</td>
</tr>
</tbody>
</table>

1.3 Synergy of this thesis

This thesis explores the assembly properties of colloidal semiconductor nanocrystals and the resulting collective properties thereof. We use two model systems, spherical quantum dots and nanoplatelets, which we assemble using solvent- or ligand-mediated interactions.

Part I of this thesis reviews the theoretical background needed to appreciate this thesis, as well as the experimental techniques used.

In chapter 2, we review the main experimental details relevant to this thesis, including experimental techniques and synthetic methods. Importantly, we discuss in detail the protocols followed for the synthesis of nearly monodisperse quantum dots and nanoplatelets.

In chapter 3, we exploit the emulsion template to drive the assembly of CdSe nanocrystals into spherical supercrystals close to single-crystal quality. By using synchrotron-based small-angle X-ray scattering, we monitor the assembly kinetics and study the kinetic detail of nucleation, growth and final densification of quantum dot supercrystals.

In chapter 4, we investigate the optical properties of single spherical supercrystals based on CdSe nanocrystals. The supercrystals sustain Mie-type modes that enhance their absorption and scattering cross sections. By combining the results of Mie optical
modeling with steady-state and transient optical spectroscopies, we conclude that the enhanced intensity of the electric field sustained within the supercrystals is largely responsible for their properties.

Part III of this thesis focuses on the surface chemistry of nanocrystals, and its influence on the assembly properties of nanoplatelets.

In chapter 5, we investigate the influence of ligand exchange with conductive thiostannate ligands on semiconductor nanoplatelets. We find that the ligand exchange process may damage nanoplatelets, and that this damage can be prevented or even reversed by a careful choice of ligand exchange conditions.

In chapter 6, we drive the assembly of nanoplatelets at the air/liquid interface in micrometer-sized patches characterized by nematic ordering. Post-assembly ligand exchange decreases the interparticle distance while maintaining the overall order. We find that nanoplatelets may also be assembled in the bulk of the solution by depletion forces, forming micrometer-long nanowires.

Part IV of this thesis is concerned with the assembly of quantum dots via solvent-mediated interactions.

In chapter 7, we drive the assembly of nanocrystals using critical Casimir forces. We show that the assembly kinetics strongly depend on the magnitude of the interaction and on the preferential wetting properties of solvent density fluctuations on quantum dot surfaces.

In chapter 8, we show that by tuning the magnitude and length scale of the critical Casimir interaction, it is possible to tune the morphology of quantum dot aggregates. This has immediate consequences on the electron mobility of critical Casimir-grown quantum dot thin films.

In chapter 9, we exploit the critical Casimir interaction between quantum dots dispersed in solution and a flat silicon substrate to drive the epitaxial growth of nanocrystals. By carefully tuning the interplay between electrostatic and critical Casimir interactions, we grow quantum dot monolayers tunable in morphology and surface coverage.

Part V concludes this thesis.

In chapter 10, we provide a summary of the content of this thesis. This is followed by a personal outlook concerning future research on nanocrystals and their assembly, chapter 11. A list of references, and of publications this thesis is based on, can be found afterwards.

An appendix now follows to discuss the Derjaguin approximation often used in chapter 1.
1.3. Synergy of this thesis

Appendix: The Derjaguin approximation

Let us assume to have two spheres of diameters $\sigma_1$ and $\sigma_2$ at a distance $d$. If $d \ll \sigma_{1,2}$ then a simple relation exists between the force between the two spheres and the interaction free energy per unit area between two planar surfaces separated by a distance $d$. This relation is general to any kind of interaction, and it is often used since it is usually easier to derive the interaction free energy for planar geometries:

$$F_{\text{spheres}}(d) = \pi \frac{\sigma_1 \sigma_2}{\sigma_1 + \sigma_2} W_{\text{planes}}(d)$$  \hspace{1cm} (1.25)

which in the symmetric case $\sigma_1 = \sigma_2 = \sigma$ simplifies to:

$$F_{\text{spheres}}(d) = \frac{\pi}{2} \sigma W_{\text{planes}}(d)$$  \hspace{1cm} (1.26)

In the framework of this approximation, known as the Derjaguin approximation, it is then possible to derive the free energy of the interaction between sphere by simply integrating afterwards:

$$\Delta U_{\text{spheres}}(d) = U_{\text{spheres}}(d) - U_{\text{spheres}}(+\infty) = \int_{+\infty}^{d} F_{\text{spheres}}(x) dx = \frac{\pi}{2} \sigma \int_{+\infty}^{d} W_{\text{planes}}(x) dx$$  \hspace{1cm} (1.27)

It is important to realize that to prove the validity of this approximation, we only need to make use of the fact that $d \ll \sigma$, with no assumptions on the nature of the interaction at play. Therefore the validity of the approximation is absolutely general, as we saw in section 1.2.