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LECTURE TEXT

# An overview of surface forces and the DLVO theory

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**Abstract**

This lecture text focuses on surface forces and interactions in a liquid medium, with particular emphasis on the surface-surface interactions described by the DLVO theory, i.e., van der Waals attraction and electric double-layer repulsion. The text begins by describing the fundamental forces of nature, their connection to intermolecular interactions, and how the latter result in measurable forces between surfaces and macroscopical objects. A step-by-step reasoning on how DLVO forces arise is then presented, accompanied by a simplified description of the mathematical derivations of the main equations within the framework of the theory. The connection between the DLVO theory and the prediction of the stability of colloidal systems is presented. Examples on how the colloidal stability can be controlled or tuned are presented. The shortcomings of the original DLVO theory are discussed, and recent extended models dealing with these issues are briefly described. The text closes with a general overview of some of the most relevant non-DLVO interaction.

**Keywords** Colloidal stability · Surface forces · Poisson-Boltzmann equation · Debye length

## Introduction

Forces and interactions between surfaces are all around us and play a vital role in our everyday life. They prevent the immediate separation of fat and water in the milk we keep in our fridges, they make it possible for us and our children to create soap bubbles to play with, they make wet floors slippery, etc. They are in fact, ubiquitous, and just as important for our daily activities as, for example, the gravitational force. Thus, many excellent books on the topic of surface-surface interactions have been written, spearheaded by Jacob Israelachvili's "Intermolecular and Surface Forces" [1]. The level of these books may, however, be considered too complicated for most undergraduate students, and there is an astonishing lack of dedicated basic textbooks on the topic. In this lecture text the origin, range and strength of surface forces will be described and the DLVO theory will be introduced to students of chemistry, biology and pharmacy. This theory provides a conceptually simple and very accurate description of how surfaces separated by a liquid interact with each other and is key to understanding, for example, the behavior of colloidal systems. As most surfaces and bodies are composed of molecules, the text will start by briefly introducing intermolecular forces and then extrapolate this to how surfaces and macroscopic objects interact with each other. The reasoning behind the classic DLVO theory as well as descriptions of novel developments in the field will also be presented. Finally, the text will briefly discuss surface forces not described by the DLVO theory.

The term "surface" in this text will be used to refer to the interface between two phases (i.e., the plane at which one material ends and the other one begins) or between a phase and a vacuum. In contrast, the term "bulk" refers to the inside of the material, where all molecules/atoms are surrounded by molecules/atoms of the same kind.

### Forces and interactions in nature

There are four fundamental interactions in nature from which all other interactions originate. These fundamental forces are:

- The weak force, acting between subatomic particles and responsible for the radioactive decay of atoms.
- The strong force that keeps quarks packed into protons, neutrons, etc., as well as binding together neutrons and protons to form atomic nuclei.

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- Gravitation, a very weak interaction acting between objects with mass and/or energy
- Electromagnetism, acting between charged particles.

Of these interactions, only gravitation and electromagnetism give rise to observable macroscopic phenomena, partly because both have infinite range (in contrast with the weak and strong interactions, which act only at extremely short separations). Of these forces, electromagnetism is the most relevant to explain chemical processes. In principle, all interactions between atoms and molecules are of electromagnetic origin. In fact, the existence of condensed phases (liquid and solid phases) is possible only thanks to the electromagnetic force acting between molecules and atoms.

## Intermolecular forces

All atoms and molecules are composed of protons and electrons, i.e., charged particles. If a molecule or atom loses or gains one or more electrons, it will acquire a charge and become an ion. The energy of interaction $W_{\mathrm{ion}}$ between ions in a medium at separations $r$ much larger than their respective radius can be described by Coulombs law:

$$W_{\mathrm{ion}}(r) = \frac{z_1 z_2 e^2}{4\pi\varepsilon\varepsilon_0 r}, \tag{1}$$

where $z_1$ and $z_2$ are the valences of the interacting ions, $e$ is the elementary charge (i.e., the charge of an electron, $1.602 \times 10^{-19}$ C), $\varepsilon_0$ is the permittivity of vacuum (a constant reflecting the ability of an electric field to pass through a vacuum, $8.854 \times 10^{-12}$ f/m), and $\varepsilon$ is the relative permittivity of the medium. The interaction is attractive if the sign for $W(r)$ is negative (i.e., if $z_1$ and $z_2$ have opposite signs) and repulsive if the sign is positive (if $z_1$ and $z_2$ have the same sign). A conclusion that can be drawn from Eq. (1) is that the interaction between two ions is long range, since its strength is directly proportional to the inverse of the distance between them. The interaction will thus be observable already at large separations. Coulomb's law describes ion-ion interactions rather accurately. It is necessary, however, to keep in mind that the equation assumes that the ions have no volume (i.e., they are treated as point charges). At very close separations (in the range of the ionic radii), other effects need to be considered.

Non-charged molecules interact with each other also via electrostatic interactions. We can consider first the interaction between polar molecules (i.e., molecules with a permanent dipol moment). The positive end of a dipole will attract the negative end of another. If the dipoles can rotate freely (as, e.g., in gas or liquid form), the dipoles will spend more time in a relative position to each other in which this attraction is maximized. Thus, the negative end of one dipole will be oriented mainly toward the positive end of another dipole, resulting in a net electrostatic attractive force between non-charged polar molecules. This interaction is known as the Keesom interaction, and it decays with the separation up to a power of six, meaning it has much shorter range than the interaction between ions.

Polar molecules and ions can also attract or repel electrons in the electron cloud of another molecule, inducing thus a dipole moment. This leads to a net electrostatic attraction, even between polar and non-polar molecules. This interaction is called the Debye interaction and decays also with the separation up to the power of six.

Finally, as all molecules and atoms are surrounded by an electron cloud in constant movement, the possibility of having an uneven distribution of electrons within the cloud at a certain given moment always exists. When this occurs, the molecule/atom will possess a dipole moment (an instant dipole). This dipole moment can induce a dipole in another molecule, thus resulting in an attractive force between molecules. This force is called “dispersion force” or London force and is found between all kinds of molecules. Dispersion forces make it possible for elements such as helium to condense into a liquid phase. The interaction has the same range as the Keesom and Debye interactions, i.e., it decays with the separation up to the power of six.

Together, the Keesom, Debye and London interactions are grouped in what is called the van der Waals interactions, a ubiquitous form of interaction between molecules. The total van der Waals interaction between two molecules in vacuum is given by the simple expression:

$$W_{\mathrm{vdW}}(r) = -\frac{C}{r^6}, \tag{2}$$

where the parameter $C$ includes the contribution from the Keesom, Debye and London interactions and is thus dependent on the permanent dipol moment, polarizability and the first ionization energy of the molecules interacting. For molecules interacting in vacuum, $C$ is always positive, meaning that the van der Waals interaction in vacuum is always attractive. In contrast with the ion-ion interaction described by Eq. (1), van der Waals interactions between molecules have a very short range. The attraction will thus only be noticeable at very short separations.

## Surface forces and DLVO theory

Atoms, molecules and ions constitute the building blocks of most materials. Even very small objects, such as, for example, colloidal particles (i.e., particles with a few nm or µm in size) contain at least several thousands and often millions/billions of such building units. The constituting molecules (or atoms) in one object interact with all molecules (or atoms) in another object via van der Waals interactions. Thus, as will be shown below, the interaction between surfaces is to a great extent defined by the van der Waals interaction between their respective components.

For surfaces interacting in a liquid medium, an entropic repulsive force (the electric double-layer repulsion) arising from electrostatic interactions between ions in the medium will also be observed. The van der Waals and electric double-layer interactions form the core of the DLVO theory, named after the scientist that developed it: Derjaguin and Landau in Russia in 1941 [2] and Verwey and Overbeek [3] in 1948 in The Netherlands.

The DLVO theory is particularly useful to describe and predict the stability of colloidal dispersions. A colloidal system is by definition composed of microscopic particles dispersed throughout a medium. How long the particles will remain dispersed is a measure of the colloidal stability of the system. The colloidal stability depends on the interplay between the attractive and repulsive forces acting between the particles. Thus, in the frame of the DLVO theory, the colloidal stability of a given system depends on the relative strengths of the attractive van der Waals and the repulsive electric double-layer interactions, which will be described in detail in the following sections.

## Van der Waals forces between surfaces

Let us imagine having an infinite planar wall. If we place a molecule at a given distance from the wall, van der Waals interactions will exist between this molecule and all the molecules forming the wall. The total energy of interaction between the molecule and the wall can be approximated as the sum of all these interactions, as proposed in the pioneering work by Hamaker [4] and Bradley [5].

To find an expression for this interaction, consider the situation depicted in Fig. 1. Here, a molecule is placed at a distance $d$ from an infinite planar wall. The position of the molecule is defined as the origin point of a Cartesian coordinate system, with the wall plane found at a distance $d$ in the $y$-axis. Consider now the interaction of the molecule with a volume differential within the wall at the coordinates $(x, y, z)$. The volume differential will be given by $\mathrm{d}V = \mathrm{d}x * \mathrm{d}y * \mathrm{d}z$, and its separation $r$ from the molecule will be given by $r = \sqrt{x^2 + y^2 + z^2}$. The van der Waals interaction between the molecule and all molecules within the volume differential will be given by:

$$\mathrm{d}W_{\mathrm{vdW}}(r) = -\rho \frac{C}{r^6}\mathrm{d}V = -\rho \frac{C}{\left(x^2 + y^2 + z^2\right)^3}\mathrm{d}x\mathrm{d}y\mathrm{d}z, \tag{3}$$

where $\rho$ is the density (in molecules per volume unit) of the wall.

Integrating over the space occupied by the wall (i.e., taking the sum of the interaction between the molecule and all possible volume differentials), an expression for the total interaction is obtained:

$$W_{\mathrm{vdW}}(r) = \int_{-\infty}^{\infty}\int_{d}^{\infty}\int_{-\infty}^{\infty} - \frac{C\rho}{\left(x^2 + y^2 + z^2\right)^3}\mathrm{d}x\mathrm{d}y\mathrm{d}z = -\frac{\pi \rho C}{6d^3}. \tag{4}$$

An interesting consequence of Eq. (4) is the fact that the strength of the interaction is observed to decrease with $d^{-3}$, in contrast with the $r^{-6}$ dependence observed between molecules. This implies that the van der Waals interaction between a molecule and infinite wall has much longer range than between single molecules.

A similar analysis can be used to estimate the total van der Waals interaction between two infinite planar walls (Fig. 2). In this case, the interaction between two volume differentials is calculated and integrated over the volume of the two walls (i.e., one calculates the sum of all possible interactions between molecules in one wall and molecules in the other one). To obtain a finite value, the interaction is calculated per unit area. The

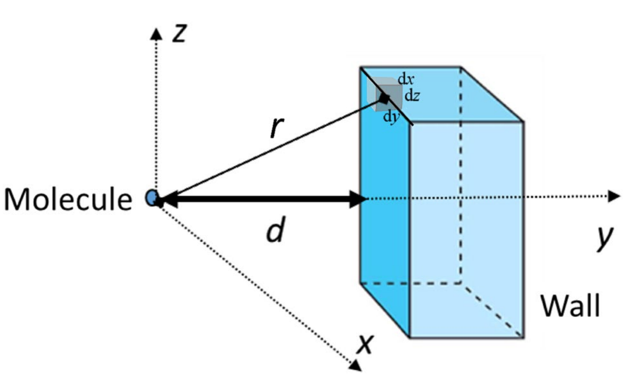


**Fig. 1** A single molecule interacting with an infinite wall

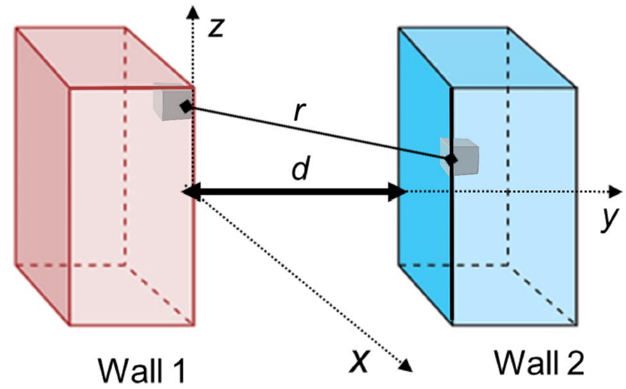


**Fig. 2** Two infinite planar walls interacting with each other

separation $r$ between volume differentials would be given by $r = \sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2}$ and thus:

$$W_{\mathrm{vdW}}(d) = \int_{-\infty}^{0} \int_{-\infty}^{\infty} \int_{d}^{\infty} \int_{-\infty}^{\infty} - \frac{C\rho_1\rho_2}{\left((x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2\right)^3} \mathrm{d}y_1 \mathrm{d}x_2 \mathrm{d}y_2 \mathrm{d}z_2 = -\frac{\pi\rho_1\rho_2 C}{12d^2} = -\frac{H_{12}}{12\pi d^2}, \quad (5)$$

where $H_{12} = \pi^2\rho_1\rho_2 C$ is the Hamaker constant describing the interaction between the two walls. Equation (5) implies that the van der Waals interaction between planar surfaces has much longer range than between molecules since its strength decreases with the square of the separation. This means that the short-range van der Waals forces acting between molecules can give rise to long-range forces between macroscopical objects.

The pairwise additivity assumptions made in the derivations above ignore, among other phenomena, the effect of atoms and molecules in the vicinity of two molecules interacting. More rigid approaches to estimate the interaction between two planar walls result, however, in an expression identical as given by Eq. (5). The only difference is the way the Hamaker constant is calculated (see, e.g., the derivation by Israelachvili [6]). Furthermore, it can be shown that the same expression can be used to describe the interactions between two objects in a medium. Again, the only difference is the value of the Hamaker constant, which will be dependent not only on the materials interacting, but also on the medium in which the interaction takes place. Thus, the interaction per unit area between Wall 1 and Wall 2 in Medium 3 (Fig. 3) is described by the equation:

$$W_{\mathrm{vdW}}(d) = -\frac{H_{132}}{12\pi d^2}. \quad (6)$$

The Hamaker constant for the interaction in a medium $H_{132}$ is related to the Hamaker constant of the different materials in vacuum as given by the combination rule: $H_{132} \approx \left(\sqrt{H_{11}} - \sqrt{H_{33}}\right)\left(\sqrt{H_{22}} - \sqrt{H_{33}}\right)$. An interesting consequence of the combination rule is that the Hamaker constant for the interaction in a medium $H_{132}$ can be negative if $H_{11} < H_{33} < H_{22}$ (or vice versa), i.e., if the value of the Hamaker constant of the medium lies between the values of the Hamaker constants of the two materials interacting. In such cases, the van der Waals interaction between the walls will be repulsive. Notice that these repulsive van der Waals interactions are possible only in a medium and only if the two materials interacting are different. Between two similar materials or between any materials in vacuum, the interaction is always attractive.

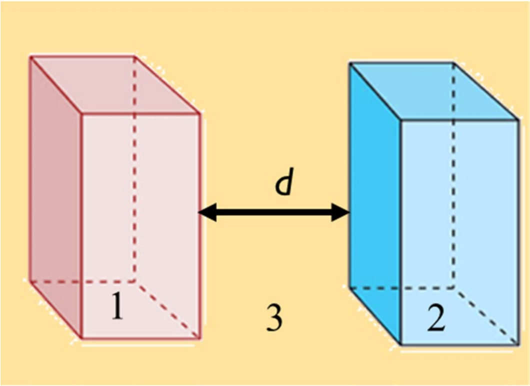


**Fig. 3** Two infinite planar walls interacting in a medium

In the frame of the DLVO theory, a final step to be able to estimate the strength of van der Waals interaction between colloidal particles is to find expressions to describe the interaction between particles with finite geometries. In particular, the interaction between spherical objects is of relevance within the field of colloids. A very useful relationship to easily determine the force $F(d)$ acting between two spheres is given by the Derjaguin approximation [7], which states that this force will be proportional to the interaction energy between two planar surfaces $W(d)$ as long as the separation $d$ between the spheres is shorter than their radii:

$$F(d) = \frac{2\pi W(d)}{(1/R_1) + (1/R_2)}, \quad (7)$$

where $R_1$ and $R_2$ are the radii of the two spheres interacting. In the case of spheres with the same radius $R$, Eq. 7 simplifies to $F(d) = \pi R W(d)$. The Derjaguin approximation applies to all kinds of interactions and is therefore very useful to extrapolate the results obtained when considering two infinite surfaces to what would be expected for two finite spheres. The energy of the interaction between two spheres $W_{\mathrm{s}}(d)$ can then be calculated from:

$$W_{\mathrm{s}}(d) = -\int_{\infty}^{d} F(d)\mathrm{d}d. \quad (8)$$

In the case of van der Waals interactions between two identical spheres with radius $R$, combining Eqs. 6, 7 and 8 gives us the expression:

$$W_{\mathrm{s(vdW)}}(d) = -\frac{H_{131}R}{12d}. \quad (9)$$

Remarkably, the van der Waals interaction between spherical particles is thus shown to decay linearly with the inverse of the separation and thus behaves similarly to the Coulomb interaction between ions (Eq. 1).

Comparing Eqs. 6 and 9 reveals that the distance dependence of van der Waals interactions varies with the geometry of the objects interacting. Thus, the range of the interaction between spherical particles is much longer than for planar surfaces and other geometries, as summarized and exemplified in Fig. 4.

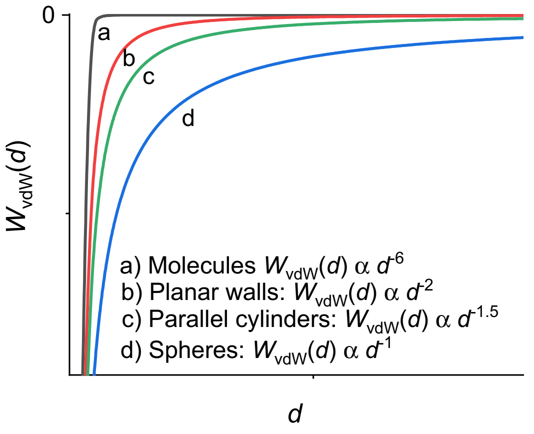


**Fig. 4** Distance dependence of the van der Waals interactions for selected geometries

## Electric double-layer repulsion between surfaces in a liquid

The second force described by the DLVO theory is the repulsion between surfaces in a liquid arising due to their respective electric double layers. As will be discussed below, this repulsion, although commonly referred to as "electrostatic," is in fact entropy-driven. Indeed, the "pure" electrostatic, energy-driven, interaction between two equally charged surfaces in a liquid is, counterintuitively, attractive. Why this is the case and what then drives the net repulsion described by the DLVO theory will be discussed in the following sections.

### Surfaces in a liquid: the electric double-layer and the Poisson-Boltzmann equation

A surface submerged in a polar liquid will probably acquire a certain electrical charge. There are several mechanisms by which surface charges appear. For example, in water and other hydrogen-bonding liquids, one can expect the dissociation of acidic or basic groups at the surface, resulting thus on the formation of, respectively, negative or positive surface charges. The surface can also acquire a charge if ions from the solution adsorb or bind onto it. What is important to keep in mind is that, regardless of how the surface acquires a charge, the solution will acquire the same amount of charges but with opposite sign, usually in the form of *counterions* such that the system in its totality remains neutral. These counterions are the complementary product of the reaction by which charges at the surface are generated. For example, in the case of dissociation of an acid at the surface:

$$-\mathrm{COOH}_{(\mathrm{surface})} \rightarrow -\mathrm{COO}^{-}_{(\mathrm{surface})} + \mathrm{H}^{+}_{(\mathrm{solution})}.$$

Thus, for every negative charge at the surface there is a positive ion in solution. Similarly, in the case of ion adsorption:

$$\mathrm{Na}^{+}_{(\mathrm{solution})} + \mathrm{Cl}^{-}_{(\mathrm{solution})} + \mathrm{bindingsite}_{(\mathrm{surface})} \rightarrow \mathrm{Na}^{+}_{(\mathrm{solution})} + \mathrm{Cl}^{-}_{(\mathrm{surface})}.$$

In this case, $\mathrm{Cl}^-$ in solution adsorbs onto a binding site on the surface, rendering the surface negatively charged. The sodium counterion remains in solution. Thus, for every negative charge that is transferred to the surface, there is a positive charge remaining in the solution.

The spatial distribution of the counterions in the liquid medium close to the surface is not random but results from a compromise between their mixing entropy (which favors a homogeneous distribution of the ions in the available volume) and the electrostatic attraction between the surface and the counterions, which favors the accumulation of counterions at the interface. Some of the ions will form a compact layer at the surface, forming a so-called Stern layer. The rest will be distributed in a "cloud" expanding from the surface, with the counterion concentration decreasing as the separation from the surface increases [8]. This forms the so-called diffuse layer (Fig. 5).

To better describe the distribution of ions in the liquid medium, it is necessary to consider that the total chemical potential $\mu$ of a single ion in the solution is given by the sum of the electrostatic and entropic contributions mentioned above:

$$\mu = ze\psi(x) + kT\ln n(x), \tag{10}$$

where $z$ is the valence of the ion, $e$ is the elementary charge, $\psi(x)$ is the electrical potential at a given position $x$ in the solution, $k$ is the Boltzmann constant ($k = 1.38065 \times 10^{-23}$ J K$^{-1}$), $T$ is the absolute temperature, and $n(x)$ is the ion concentration at position $x$. At equilibrium, the chemical potential $\mu$ of the ion must be the same at all values of $x$. Given that only electrical potential differences (and not absolute values of the electrical potential) are ever meaningful, we can define an arbitrary position $x$ where the potential is set to $\psi = 0$ and the ion concentration is thus $n_{(\psi=0)}$. From Eq. 10, it can then be shown that $n(x)$ is given by the Boltzmann distribution:

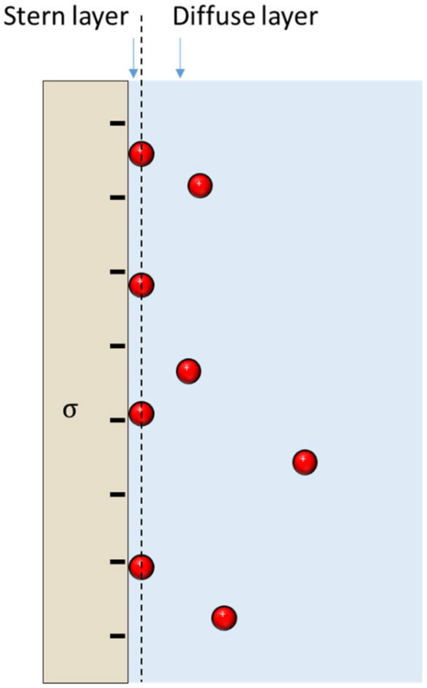


**Fig. 5** Depiction of a negatively charged wall with surface charge density σ immersed in a liquid. A compact layer of counterions form close to the surface (Stern layer). The rest of the counterions are distributed in a diffuse layer

$$n(x) = n_{(\psi=0)} \mathrm{e}^{-\frac{ze\psi(x)}{kT}}. \tag{11}$$

A second needed relationship between the ion concentration and the potential can be derived from the Poisson equation, which states that:

$$\rho(x) = -\varepsilon\varepsilon_0 \frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2}, \tag{12}$$

where $\rho(x)$ is the bulk charge density, roughly defined as the "charge concentration," at position $x$ and given by:

$$\rho(x) = e\sum z_i n_i(x). \tag{13}$$

Combining Eqs. 11, 12 and 13, one obtains the Poisson-Boltzmann (PB) equation:

$$\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} = -\frac{e}{\varepsilon\varepsilon_0}\sum z_i n_{i(\psi=0)} \mathrm{e}^{-\frac{z_i e\psi(x)}{kT}}. \tag{14}$$

By applying appropriate limiting conditions, Eq. 14 can be used to determine the potential $\psi(x)$, ion concentration $n(x)$ and electric field $E(x) = |\mathrm{d}\psi(x)/\mathrm{d}x|$ at any point $x$ near a charged surface, or, more importantly for the purpose of this text, at any point $x$ in between two surfaces. The equation thus lies at the heart of the DLVO theory.

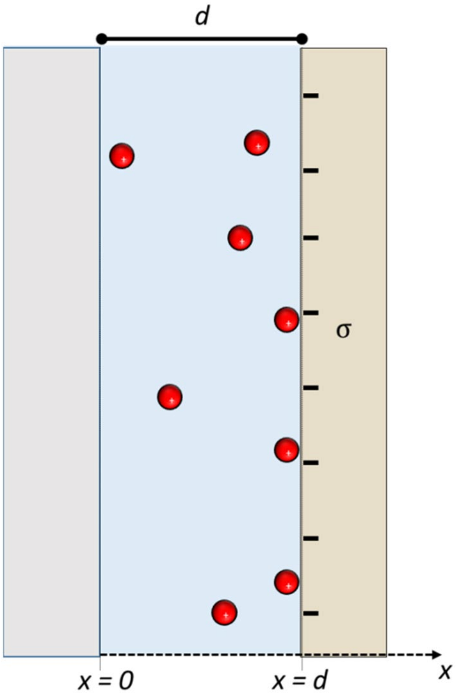


**Fig. 6** Representation of a neutral surface placed at a separation $d$ from a negatively charged surface with surface charge density σ

## Electric double-layer interaction between a charged and a neutral planar wall in the absence of electrolyte

Consider the situation depicted in Fig. 6, where a non-charged planar wall is placed at $x=0$ and a charged planar wall with a surface charge density $\sigma$ is placed at $x=d$. Counterions accumulate in the gap between the walls, ensuring thus electroneutrality. Imagine now that outside of the gap there is a reservoir of solvent in which no ions are present. The mixing entropy of the trapped counterions would increase if the solvent from the reservoir would flow in the gap, effectively pushing the walls apart. Thus, a repulsive osmotic pressure acts at all points within the gap. This pressure is highest at the vicinity of the charged surface (at $x=d$, where the concentration of ions is highest) and lowest right next to the uncharged surface (at $x=0$). An opposing, attractive pressure is also found in the gap, and it has an electrostatic (enthalpic) origin: counterions in solution are attracted to the charged wall (and vice versa) and thus they effectively pull the walls together. This pressure is also highest at $x=d$, and it is zero right at the interface between the medium and the uncharged wall (i.e., at $x=0$) since the latter experiences no electrostatic pull. The total pressure $P_{\mathrm{DL}}(d)$ is the sum of both these contributions, and it should be uniform across the gap. Since the electrostatic contribution at $x=0$ is zero, the total pressure acting in the system is given by the osmotic pressure at this point, i.e.:

$$P_{\mathrm{DL}}(d) = kTn_0, \tag{15}$$

where $n_0$ is the concentration of counterions at $x = 0$. This concentration will be dependent on the separation $d$ between the walls.

To be able to calculate the value of the pressure acting between the walls, $n_0(d)$ needs to be determined. This can be done with help of the PB equation (Eq. 14), which, for the system depicted in Fig. 6, becomes:

$$\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} = -\frac{e}{\varepsilon\varepsilon_0} z n_0 \mathrm{e}^{-\frac{ze\psi(x)}{kT}}, \tag{16}$$

where the potential at $x = 0$ has been set to zero (i.e., $\psi(0) = 0$). A further limiting condition needed to solve Eq. (16) is given by the electric field at $x = 0$, which is zero, i.e.,$E(0) = |\mathrm{d}\psi(x)/\mathrm{d}x|_{x=0} = 0$

The solution to Eq. 16 is thus (see Engström et al. [9]):

$$\psi(x) = \frac{2kT}{ze} \ln(\cos(Kx)), \tag{17}$$

where

$$K = ze\sqrt{\frac{n_0}{2kT\varepsilon\varepsilon_0}}. \tag{18}$$

As stated above, the electroneutrality condition must be fulfilled, i.e., that the surface charge density must be compensated by the sum of the bulk charge densities at all positions in the gap, i.e.:

$$\sigma = -\int_0^d \rho(x)\mathrm{d}x = \varepsilon\varepsilon_0 \int_0^d \left(\frac{\mathrm{d}^2\Psi(x)}{\mathrm{d}x^2}\right)\mathrm{d}x = \varepsilon\varepsilon_0\left(\left(\frac{\mathrm{d}\Psi(x)}{\mathrm{d}x}\right)_{x=d} - \left(\frac{\mathrm{d}\Psi(x)}{\mathrm{d}x}\right)_{x=0}\right) = \varepsilon\varepsilon_0(E(d) - E(0)) = \varepsilon\varepsilon_0 E_{\mathrm{s}}, \tag{19}$$

where $E_{\mathrm{s}} = E(d)$ is the electric field directly at the surface of the charged wall. Combining Eqs. 17 and 19, one obtains:

$$E_{\mathrm{s}} = \left|\frac{\mathrm{d}\Psi(x)}{\mathrm{d}x}\right|_{x=d} = -\frac{2kTK}{ze}\tan(Kd) = \left|\frac{\sigma}{\varepsilon\varepsilon_0}\right|. \tag{20}$$

For a given system where $\sigma$ is known, $n_0$ can be numerically determined for a given $d$ using Eq. 20, thus allowing calculating the pressure acting between the surfaces.

## Electric double-layer interaction between two identical charged infinite walls in the absence of electrolyte

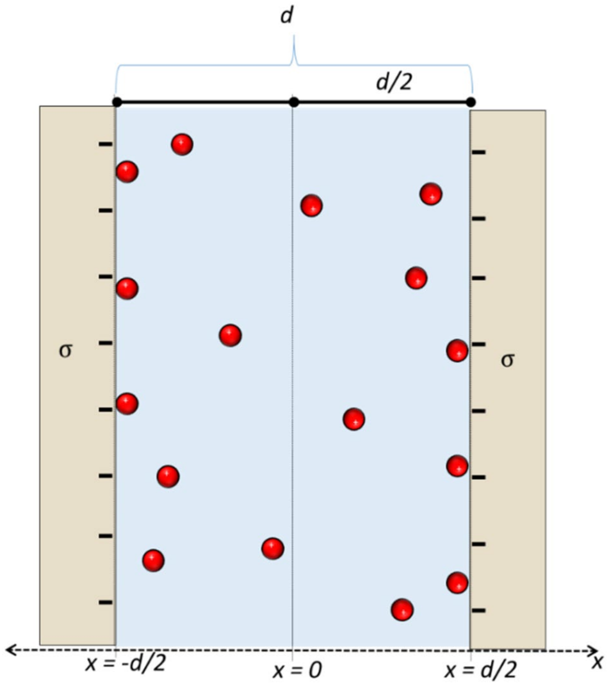


**Fig. 7** Representation of two identical charged walls placed at a separation $d$ from each other

Consider now two identical charged walls interacting in a liquid. In this case, the electrostatic contribution to the total pressure will be zero right at the midplane, and the pressure acting between the walls is thus given by the concentration of ions at this point [9]. It is thus convenient to set $x = 0$ and $\psi = 0$ at the midplane. The charged surfaces are thus located at $x = \pm(d/2)$, as depicted in Fig. 7. Each half of the system depicted in Fig. 7 is identical to the system illustrated in Fig. 6, with the neutral surface being replaced by the midplane. The solution for the PB equation is thus similar to the case described above. The only difference is that the separation $d$ in Eq. 20 must be replaced by $d/2$ [9]:

$$E_{\mathrm{s}} = -\frac{2kTK}{ze}\tan\left(K\frac{d}{2}\right) = \left|\frac{\sigma}{\varepsilon\varepsilon_0}\right|. \tag{21}$$

Thus, two charged surfaces separated by a distance $d$ will interact with the same strength as a charged and a neutral surface separated by $d/2$ [10].

## Isolated charged surfaces in an electrolyte solution

The cases described in the previous sections are unlikely to be found in real systems, particularly if water is the medium. In such case, most surfaces will acquire a charge, and there will always be other ions in solution besides the surface counterions. All these ions need to be considered when solving the PB equation. For two surfaces interacting in an electrolyte, the approach used in previous cases does not provide an analytical solution concerning the concentration of ions at any point in the gap. Instead, it becomes necessary to

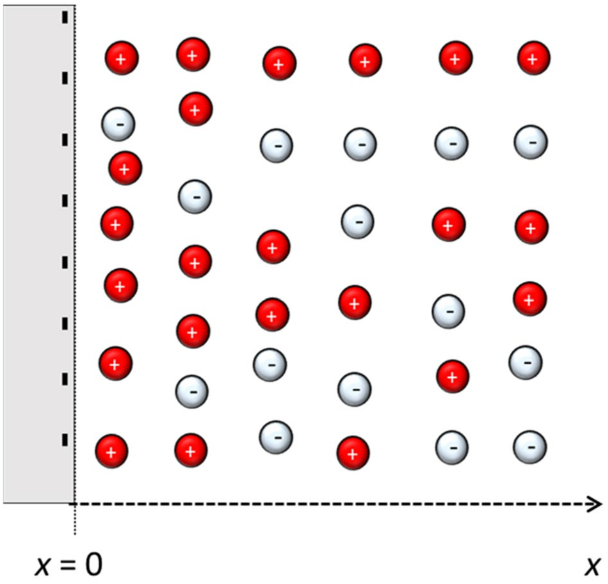


**Fig. 8** Representation of an isolated charged wall in an electrolyte solution

treat each wall as an isolated surface and to define $\psi = 0$ at a point where the concentration of the ions is known. Thus, $x = 0$ is defined right at the surface of the wall, and $\psi = 0$ is set at $x = \infty$ (see Fig. 8). Thus, $n_{(\psi=0)} = n_{(x=\infty)}$, i.e., the concentration of ions at an infinite separation from the surface. This is equal to the bulk concentration of ions.

The solution to the PB equation (Eq. 14) becomes much more cumbersome when an electrolyte solution is present. Table 1 summarizes the expressions for $\psi(x)$ obtained for symmetrical electrolytes (i.e., electrolytes where the anion and the cation have the same absolute valence $z$) and for a mixture of 2:1 (e.g., $CaCl_2$) or 1:2 (e.g., $Na_2SO_4$) with a 1:1 (e.g., NaCl) electrolyte. The equations are expressed in terms of the parameters $\psi_0$ and $n_{i(\infty)}$, which represent, respectively, the *surface potential* (i.e., the potential at $x = 0$) and the bulk concentration of the ion $i$. In both equations, the decay of the potential as the distance from the surface increases is described by a parameter $\kappa$ dependent only on the composition and temperature of the electrolyte and not on the properties of the surface. The inverse of this parameter (i.e., $\kappa^{-1}$) is known as the *Debye length* and is a measure of the *thickness* of the electric double layer. Increasing the ionic strength of the solution decreases the magnitude of the Debye length, meaning that the electric double layer becomes thinner. Adding an electrolyte will indeed cause an increase of the counterion concentration near the surface, screening the surface charges already at small values of $x$.

The second equation in Table 1 is reduced to the first one when $a = \infty$ (i.e., when only the monovalent electrolyte is present). Setting $a = 0$ (i.e., when only the asymmetrical electrolyte is present) results in the equation proposed by Andrietti et al. [11] for the case of 2:1 (or 1:2) electrolytes, which is in turn similar to the solutions given by Grahame [12].

A relationship between the surface potential $\psi_0$ and the surface charge density $\sigma$ can be obtained from the PB equation by considering that electroneutrality is required:

$$\begin{aligned}\sigma &= -\int_0^\infty \rho(x)\mathrm{d}x = \varepsilon\varepsilon_0 \int_0^\infty \left(\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2}\right)\mathrm{d}x \\ &= -\varepsilon\varepsilon_0 \left(\frac{\mathrm{d}\psi(x)}{\mathrm{d}x}\right)_{x=0} \\ &= \sqrt{2\varepsilon\varepsilon_0 kT \sum n_{i(\infty)}\left(\mathrm{e}^{-\frac{z_i e\psi_0}{kT}} - 1\right)}.\end{aligned} \tag{22}$$

Equation 22 and the equations in Table 1 can be dramatically simplified when the value of the surface potential is low. For absolute values of $\psi_0 \ll kT/(ze)$ (the so-called "Debye approximation"), the equations in Table 1 are both reduced to:

$$\psi(x) = \psi_0 \mathrm{e}^{-\kappa x}. \tag{23}$$

Equation 23 is called the Debye-Hückel equation and is a very useful approximation valid for all kinds of electrolytes. The equation results in a very exact description of the potential decay near the surface when the surface potential is low ($<25$ mV at room temperature) as long as the surface potential and the Debye length are determined accurately; see Fig. 9 (left). Even at large surface potentials, the differences between the predictions from Eq. 23 and from the equations show in Table 1

**Table 1** Solutions of the PB equation for a symmetrical electrolyte (known as the Gouy-Chapman theory) and for a mixture of 2:1 (or 1:2) and 1:1 electrolytes mixed at a ratio $a = n_{(1:1)(\infty)}/n_{(2:1)(\infty)}$ according to unpublished work by the author

| Electrolyte | Potential |
|---|---|
| Symmetrical[a,b] | $\psi(x) = \frac{2kT}{ze}\ln\left(\frac{1+\gamma\mathrm{e}^{-\kappa x}}{1-\gamma\mathrm{e}^{-\kappa x}}\right)$ |
| Mixed 2:1 (or 1:2) and 1:1 (common monovalent ion)[b,c] | $\psi(x) = (\pm)\frac{kT}{e}\ln\left(\frac{1}{(2+a)}\left(\left(\frac{1+\beta\mathrm{e}^{-\kappa x}}{1-\beta\mathrm{e}^{-\kappa x}}\right)^2(3+a) - 1\right)\right)$ |

[a] $\gamma = \tanh\left(\frac{ze\psi_0}{4kT}\right)$

[b] $\kappa = \sqrt{\frac{e^2}{\varepsilon\varepsilon_0 kT}\sum n_{i(\infty)} z_i^2}$

[c] $\beta = \frac{\sqrt{(2+a)\mathrm{e}^{(\pm)\frac{e\psi_0}{kT}}+1} - \sqrt{3+a}}{\sqrt{(2+a)\mathrm{e}^{(\pm)\frac{e\psi_0}{kT}}+1} + \sqrt{3+a}}$

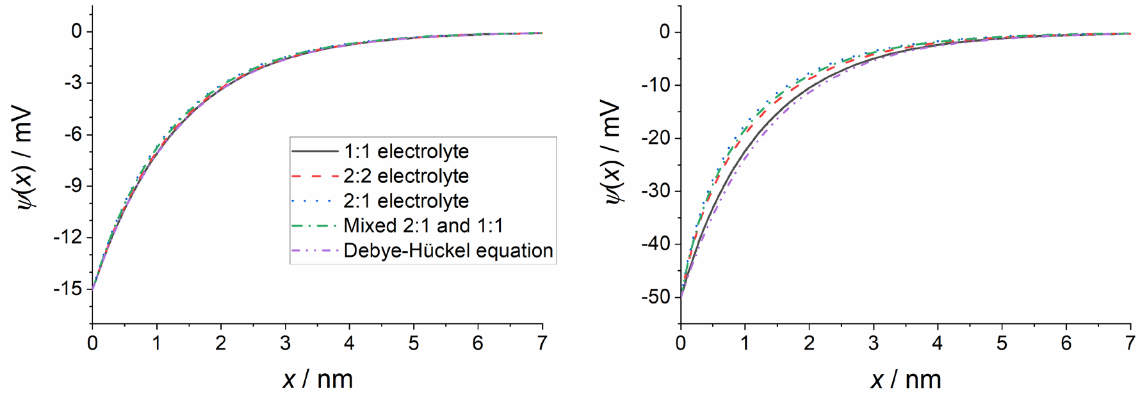


**Fig. 9** Comparison of the predictions of exact solutions to the PB equation for different electrolytes and the Debye-Hückel approximation. The Debye length is set equal in all systems (1.34 nm). Left: Surface potential: − 15 mV. Right: Surface potential − 50 mV. The legend is valid for both figures

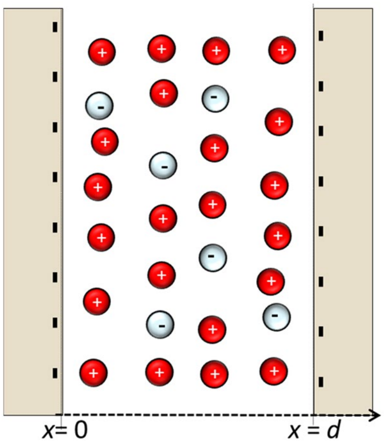


**Fig. 10** Representation of two identical charged walls placed at a separation $d$ from each other in an electrolyte solution

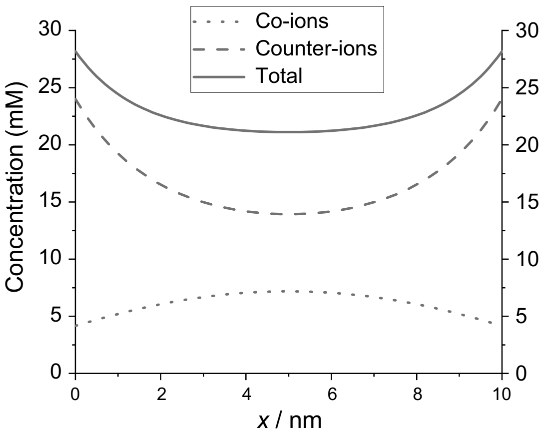


**Fig. 11** Distribution of ions in the gap between two charged surfaces ($\sigma$ = 5 mC/m.$^2$) placed at a separation $d$=10 nm in an electrolyte (NaCl 10 mM)

differ only slightly (see Fig. 9, right). For 1:1 electrolytes, the deviation is actually negligible. To simplify the description of the electric double-layer interaction between surfaces, in the following sections the Debye-Hückel equation will be used instead of the exact solutions in Table 1.

From Eq. 23, a simple relationship between the surface potential and the surface charge density is obtained:

$$\sigma = -\varepsilon\varepsilon_0\left(\frac{\mathrm{d}\psi(x)}{\mathrm{d}x}\right)_{x=0} = \varepsilon\varepsilon_0\kappa\psi_0. \tag{24}$$

## Electric double-layer interaction between two identical charged surfaces in an electrolyte solution

When considering the interaction between two charged walls in an electrolyte, it is necessary to determine how the ions distribute in the gap. The Boltzmann distribution can be used to determine the concentration at any point in between the surfaces. The potential at any position can be estimated by the *weak overlap approximation* which considers that the potential at any point in the gap between the walls will be given by the sum of the potentials of each wall treated separately. From the Debye approximation, the potential at any point $x$ between two similar walls (see Fig. 10) with a surface potential $\psi_0$ at a separation $d$ is:

$$\psi(x) = \psi_0\left(\mathrm{e}^{-\kappa x} + \mathrm{e}^{-\kappa(d-x)}\right) = \frac{\sigma}{\varepsilon\varepsilon_0\kappa}\left(\mathrm{e}^{-\kappa x} + \mathrm{e}^{-\kappa(d-x)}\right). \tag{25}$$

From Eqs. 11 and 25, the ion distribution in the gap can be calculated. Figure 11 shows the distribution of co- and counterions in the gap between two surfaces, as well as the total concentration of ions at different points in the gap:

As can be observed, the total concentration of ions is higher near the walls and lowest at the midplane. The midplane concentration is, however, higher than the bulk concentration (20 mM in the case illustrated in Fig. 11). The total pressure acting between the walls will be given by the difference between the osmotic pressure at the midplane, where the electrostatic contribution is zero, and at the bulk, i.e.:

$$P_{\mathrm{DL}}(d) = kT\left(\sum n_i(d/2) - \sum n_{i(\infty)}\right), \tag{26}$$

Substituting the Boltzmann distribution (Eq. 11) in Eq. 26, we obtain:

$$P_{\mathrm{DL}}(d) = kT\sum\left[n_{i(\infty)}\left(\mathrm{e}^{-\frac{z_i e\psi_{d/2}}{kT}} - 1\right)\right], \tag{27}$$

where $\psi_{d/2}$ is the potential at the midplane. Expanding the exponents into series, and assuming that the value of $\psi_{d/2}$ is small, Eq. 30 simplifies into:

$$P_{\mathrm{DL}}(d) = \frac{\varepsilon\varepsilon_0\kappa^2}{2}\psi_{d/2}^2. \tag{28}$$

The midplane potential $\psi_{d/2}$ calculated from the Debye and weak overlap approximations is:

$$\psi_{d/2} = 2\psi(d/2) \approx 2\psi_0\mathrm{e}^{-\frac{\kappa d}{2}}, \tag{29}$$

The pressure is thus given by:

$$P_{\mathrm{DL}}(d) = 2\varepsilon\varepsilon_0\kappa^2\psi_0^2\mathrm{e}^{-\kappa d} = \frac{2\sigma^2}{\varepsilon\varepsilon_0}\mathrm{e}^{-\kappa d}. \tag{30}$$

The energy of interaction per unit area $W(d)$ can be obtained by integration of Eq. 30. In terms of the surface charge density, one obtains:

$$W_{\mathrm{DL}}(d) = -\int_{\infty}^{d} P_{\mathrm{DL}}(d)\mathrm{d}d = \frac{2\sigma^2}{\kappa\varepsilon\varepsilon_0}\mathrm{e}^{-\kappa d}. \tag{31}$$

Using the Derjaguin approximation, the force $F_{\mathrm{s(DL)}}$ and the energy of interaction $\mathrm{W}_{\mathrm{s(DL)}}$ between spherical particles can thus be expressed as:

$$F_{\mathrm{s(DL)}}(d) = \frac{2\pi R\sigma^2}{\kappa\varepsilon\varepsilon_0}\mathrm{e}^{-\kappa d}, \tag{32}$$

and

$$W_{\mathrm{s(DL)}}(d) = \frac{2\pi R\sigma^2}{\kappa^2\varepsilon\varepsilon_0}\mathrm{e}^{-\kappa d}, \tag{33}$$

respectively. The relevance of Eqs. 30–33 is that they are valid in all kinds of electrolytes, including mixtures, as long as the Debye approximation holds. Indeed, at absolute values of $\psi_0 \ll kT/(ze)$ (around 25 mV for a 1:1 electrolyte at room temperature), the equations give a very exact description of the experimental observations as long as the Debye length is determined with precision. For larger potentials, the approximation is still rather good qualitatively, although it should be used with caution.

For more accurate results with symmetrical electrolytes, the weak overlap approximation and the corresponding equation in Table 1 can be used to get an expression for $\psi_{d/2}$. The resulting expression for the pressure acting between the surfaces is slightly more complicated than Eq. 30, but can still be integrated to obtain the energy of interaction.

For asymmetrical electrolytes or for mixtures, an equation for the pressure between walls can be obtained. However, this expression cannot always be integrated analytically to estimate the energy of interaction. Numerical approximations are thus often needed.

Summarizing the discussion above, the repulsion acting between two charged surfaces in a liquid is driven by entropy and not by a direct electrostatic repulsion between them. Indeed, purely electrostatic interactions would result in an attractive force, since the counterions attract the surface towards them. The entropy contribution as predicted by the PB equation is, however, always dominant. In Sect. "Shortcomings of the PB equation" below, examples where the electrostatic contribution actually dominates (leading to an attractive force) will be discussed.

## The total interaction between surfaces in an electrolyte

For two surfaces interacting in a liquid, the total interaction between them will be a combination of the electric double-layer repulsion and van der Waals attraction. Simply put, the total interaction is the sum of the contributions of both phenomena. For spherical particles interacting in an electrolyte solution, the total interaction is then obtained by adding Eqs. 9 and 33:

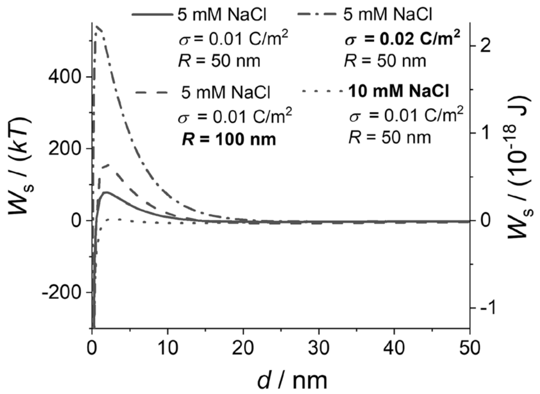


**Fig. 12** Total DLVO energy of interaction between two spherical particles as a function of separation under different conditions

$$W_{\mathrm{s(total)}}(d) = W_{\mathrm{s(DL)}}(d) + W_{\mathrm{s(vdW)}}(d) = \frac{2\pi R\sigma^2}{\kappa^2\varepsilon\varepsilon_0}\mathrm{e}^{-\kappa d} - \frac{H_{131}R}{12d}. \tag{34}$$

The effect of ionic strength, particle size and surface charge density on the total interaction at different separations is illustrated in Fig. 12. In general, the attractive van der Waals interaction is expected to dominate at short separations, since its strength tends to infinity as the separation decreases.

As observed in Fig. 12, at high surface charge densities and low ionic strengths a repulsive energy barrier appears. To come in contact with one another, two particles dispersed in a medium would need to collide with enough energy to overcome this barrier. The particles are then said to have *coagulated*, i.e., they have aggregated irreversibly. Decreasing the surface charge density or increasing the ionic strength results in a decrease (or complete vanishing) of the repulsive barrier, thus making it easier for particles to coagulate.

In cases where the magnitude of the Debye length is small, it is possible for the attractive interaction to have longer range than the repulsion. In such cases, a secondary minimum can appear (see Fig. 13). Particles trapped in the secondary minimum are said to have flocculated, i.e., they have reversibly aggregated. Flocculation in a colloidal dispersion can be observed only if the secondary minimum is deep enough to prevent both re-dispersion and coagulation. According to Eq. 34, the depth of the minimum is proportional to the size of the particles; thus, large particles are more prone to flocculate than smaller ones (Fig. 13).

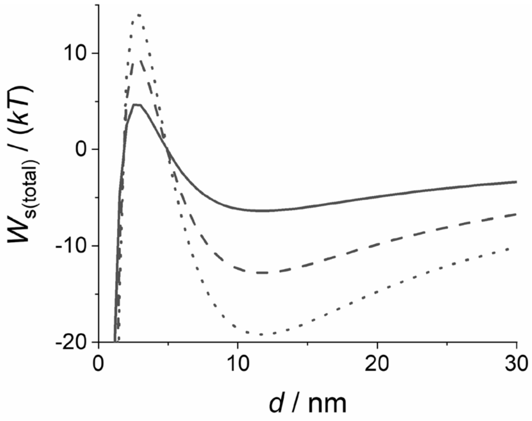


**Fig. 13** Total DLVO interaction between particles showing a secondary minimum. Electrolyte solution: 10 mM $\mathrm{NaCl_{(aq)}}$ at 25 ℃. $\sigma$ = 10 mC/m$^2$. $H_{131} = 2 \times 10^{-19}$ J. Solid line: $R = 50$ nm. Dashed line: $R = 100$ nm. Dotted line: $R = 150$ nm

## Colloidal stability and rate of coagulation

In the absence of a repulsive energy barrier, two particles approaching each other would always coagulate. When a barrier is present, it is required that the particles approach with enough energy to overcome the barrier. The proportion of particle-particle collisions with high enough energy is given by the Boltzmann factor $\mathrm{e}^{-\frac{W_{\max}}{kT}}$, where $W_{\max}$ is the height of the energy barrier. The second order coagulation rate constant is thus given by an expression resembling the Arrhenius equation:

$$k_{\mathrm{coag}} = k_0 e^{-\frac{W_{\max}}{kT}}, \tag{35}$$

where $k_0$ is the expected frequency of collisions per particle concentration. The frequency of collisions is in turn dependent on how the particles diffuse, so $k_0$ can be defined as the rate constant of a diffusion controlled process:

$$k_0 = 8\pi N_{\mathrm{A}} DR = \frac{4N_{\mathrm{A}}kT}{3\eta}, \tag{36}$$

where $D$ is the diffusion coefficient of a particle with radius $R$ and $N_{\mathrm{A}}$ is the Avogadro number ($N_{\mathrm{A}} = 6.022 \times 10^{23}$ mol$^{-1}$). The last equality in Eq. 36 is obtained from the Stokes-Einstein relationship ($D = kT/(6\pi\eta R)$, where $\eta$ is the mediums viscosity).

The rate of coagulation is given by:

$$v_{\mathrm{coag}} = k_{\mathrm{coag}}[\mathrm{B}]^2. \tag{37}$$

The coagulation frequency, defined as the number of irreversible associations per time unit is defined as $k_{\mathrm{coag}}[\mathrm{B}]$. In water at room temperature, the value of $k_0$ estimated from Eq. 36 is $3.306 \times 10^9$ L mol$^{-1}$ s$^{-1}$. This means that, in a very concentrated colloidal dispersion with [B] = 1 mol particles per liter, there will be 3.306 billion particle-particle collisions every second. How many of these collisions will result in coagulation of the colliding particles depends on the height of the energy barrier and is given by the Boltzmann factor. For a low barrier with a height of $10kT$, the Boltzmann factor is $\mathrm{e}^{-10} = 4.54 \times 10^{-5}$, resulting in a coagulation frequency of $3.306 \times 10^9 * 4.54 \times 10^{-5} \approx 150{,}000$ associations per second. For a higher barrier of about $50kT$ the Boltzmann factor is much smaller ($1.93 \times 10^{-22}$), resulting in only $6.612 \times 10^{-13}$ associations per second. The inverse of the coagulation frequency can be understood as the average time that it would take for coagulation to start happening (average time until the first association occurs). For the former case ($W_{\max} = 10kT$), this implies that the process of coagulation starts already 6.7 µs after the dispersion has been prepared, whereas, for the latter case ($W_{\max} = 50kT$), one would need to wait ~ 48,000 years in average for coagulation to start! How long a time a colloidal dispersion is expected to remain dispersed is a measure of its *colloidal stability*. Thus, a system where [B] = 1 M and $W_{\max} = 50kT$ is said to have an excellent colloidal stability, whereas if the energy barrier is reduced to $10kT$ the system is deemed unstable.

As seen in Fig. 12 above, even moderate surface charge densities can give rise to energy barriers with a height of several hundred times $kT$, resulting in good colloidal stability even at very high particle concentrations. The height of the energy barrier can, however, decrease if, for example, the surface charge density is reduced (see Fig. 12). This can be achieved by changing the dispersion pH. Usually, the surface charge density of negatively charged surfaces would decrease if the pH is lowered, leading to protonation of the charged groups. Increasing the pH would have a similar effect on positively charged surfaces. Thus, a way of controlling the colloidal stability is to adjust the pH of the dispersing media.

Another common way of decreasing the colloidal stability of a given system is to increase the ionic strength of the dispersion medium. Figure 14 shows the calculated total interaction between two particles at different concentrations of a 1:1 and a 2:2 electrolyte, respectively. As can be seen, increasing the electrolyte concentration leads to a decrease of the energy barrier, eventually resulting in $W_{\max} = 0$. The minimum electrolyte concentration at which the barrier vanishes is called the critical coagulation concentration (c.c.c.). At this electrolyte concentration (and higher), it is expected that all collisions will lead to association, causing immediate coagulation. As the figure shows, divalent electrolytes are much more effective in decreasing the energy barrier. Indeed, the so-called Schulze-Hardy rule states that the c.c.c can be proportional to $z^{-6}$ in certain cases, meaning that multivalent ions are much more effective than monovalent at inducing coagulation.

In summary, the colloidal stability (or lack of it) is the result of an interplay between the attractive van der Waals and the repulsive electric double-layer interactions. The latter can be to an extent tuned, since the main parameters affecting it (i.e., the surface charge density and the ionic strength) can often be controlled. To better illustrate how the colloidal stability is affected by these factors, two short demonstrations are included as supplementary material. The first video (Online Resource 1) illustrates how a change in pH can lead to immediate coagulation in an initially stable dispersion. The second one (Online Resource 2) shows how fast coagulation can be induced by increasing the ionic strength of the dispersion.

## The zeta potential

The colloidal stability of a given system can be predicted from the above equations if either the surface charge density or the surface potential is known. However, these parameters are not always readily available. A related parameter which is easily determined experimentally is the zeta potential (also called the electrokinetic potential). When a charged particle moves in a liquid medium, part of the diffuse layer will move with it. A slipping plane or plane of shear is defined at the boundary between the liquid "fixed" to the surface and the mobile fluid. The zeta potential is the electrical potential at this plane. Although the plane of shear is not located right at the particle surface, the magnitude of the zeta potential is related to the magnitude of the surface potential as long as no ion adsorption or condensation on the surface occurs. The advantage of the zeta potential is that it is easily measured, for example, by determining the electrophoretic mobility of the particles and using Henry's equation [13]:

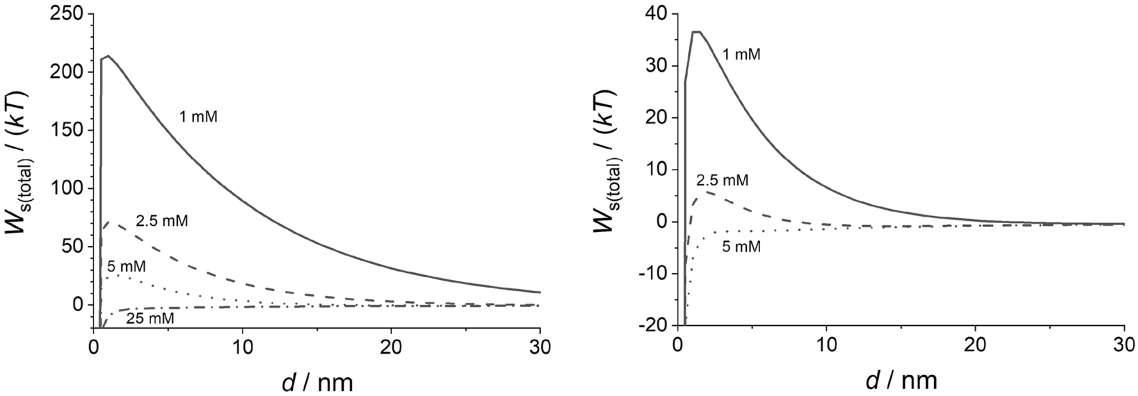


**Fig. 14** Total DLVO interaction between particles in different electrolyte concentrations. $\sigma$ = 5 mC/m$^2$, $R$ = 50 nm, $H_{131}$ = 1.5 × 10$^{-20}$ J. Left: 1:1 electrolyte. Right: 2:2 electrolyte

$$U_E = \frac{2\varepsilon\xi f(\kappa R)}{3\eta}, \quad (38)$$

where $U_E$ is the electrophoretic mobility, $\xi$ is the zeta potential, and $f(\kappa R)$ is the Henry's function, whose value is dependent on the product $\kappa R$ (i.e., on the ratio between the particle radius and the Debye length). For large particles in an electrolyte solution (i.e., for $\kappa R \gg 1$, also called the Smoluchowski limit [14]), the value of $f(\kappa R)$ approaches 1.5. For small particles in a medium with a low relative permittivity ( i.e., for $\kappa R \ll 1$, called the Hückel limit), the value of the function approaches 1. For intermediate values of $\kappa R$, more exact solutions can be obtained [15].

The magnitude of the zeta potential can be used to estimate how good the colloidal stability of a given system will be. The higher the magnitude of the zeta potential, the better the colloidal stability. A rule of thumb is that absolute zeta potential values > 30 mV will result in good colloidal stability, whereas lower values will result in flocculation and/or coagulation [16]. This general rule needs however to be used with caution, since other forces not considered by the DLVO theory can also play a role concerning colloidal stability.

## Extended DLVO theory and non-DLVO interactions

### Shortcomings of the PB equation

The DLVO theory has been repeatedly shown to accurately describe the interaction between surfaces in a liquid. The development of instrumentation such as the surface force apparatus [17] and the atomic force microscope [18] has allowed measuring the force acting between surfaces with very high precision, and in several cases the DLVO theory has been corroborated. However, clear deviations from the predicted behavior have also been observed, particularly at short separations between surfaces. Some of these deviations from the expected behavior can be attributed to assumptions made by the PB equation, among others:

- The dispersion medium is treated as a dielectric continuum,
- Ions are treated as point charges (i.e., their size is ignored),
- Interactions between ions across the midplane are ignored, i.e., the electrostatic interaction between the two halves of the system is considered to be zero since each half is considered to be electrically neutral.

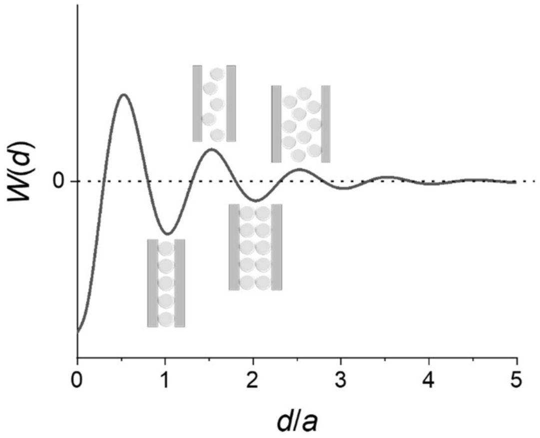


Fig. 15 Oscillatory interaction due to molecular ordering effects. Values in the $x$-axis are normalized against the molecular diameter "$a$" of the solvent

Concerning the first point, at very short separations (4–5 times the molecular diameter of the solvent) molecular ordering effects not predicted by the DLVO theory have been observed [19]. At separations corresponding to a multiple of the molecular diameter of the solvent, an interaction minimum is observed, since the solvent molecules can be packed tightly in the gap. Separating or bringing the surfaces closer together would result in non-optimal packing of the solvent molecules and thus both processes imply an energy cost. This results in an oscillatory interaction (i.e., alternating between repulsive or attractive depending on the separation) caused by the ordering of solvent molecules in between the surfaces, as illustrated in Fig. 15. The effect of molecular ordering of the solvent is only important if the surfaces interacting are very smooth and the solvent molecules are symmetrical, spherical or linear. In other cases, these effects are mostly negligible or limited to separations corresponding to 1–2 molecular diameters.

Concerning the effect of the ion size, the most readily apparent consequence of the assumption of point charges made by the PB equation is that the ion concentration at the surface can be heavily overestimated, since it is considered to increase continuously all the way down to $x = 0$. However, the fact that ions occupy a certain volume requires that no charges are present in the compact Stern layer (unless ion adsorption occur). In other words, the PB equation is formally valid only from the Stern layer onwards, and not from the surface itself. For low surface charge densities and low concentrations of monovalent electrolytes, the Stern layer is usually very thin, and the PB equation is thus valid. For high surface charge densities and heavily hydrated counterions (e.g., multivalent counterions), deviations from the PB equation at short separations can be very significant. The situation is even more complicated if specific adsorption of ions occur: adsorption of co-ions result in an increase of the magnitude of the potential across the Stern layer instead of

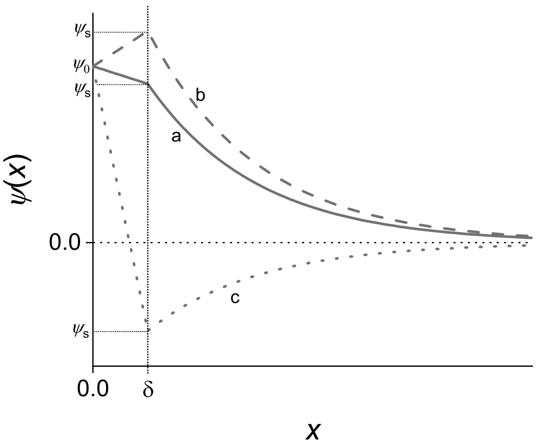


**Fig. 16** Potential as a function of the distance $x$ in the presence of a Stern layer with thickness δ **a** without adsorption of ions, **b** with adsorption of coions, **c** with adsorption of counterions, leading to inversion of polarity. The PB equation is valid only for $x > \delta$

the decrease predicted by the PB equation. Adsorption of counterions can, on the other hand, lead to charge reversal, meaning that the polarity of the Stern potential is of opposite sign to that of the surface. These different effects are illustrated in Fig. 16. In these cases, it is of the utmost importance to use the Stern potential $\psi_s$ instead of the surface potential when performing calculations on colloidal stability using the equations above.

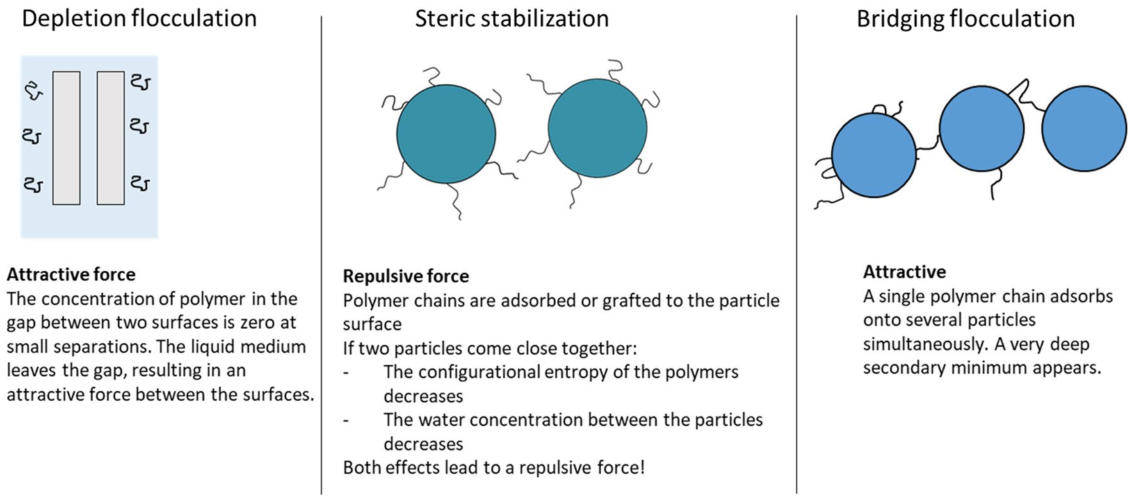
The Stern layer can also give rise to other repulsive interactions not considered by the DLVO theory, particularly at short separations. Consider, for example, two surfaces at a separation equal to twice the thickness of their respective Stern layers. Decreasing the separation between the surfaces would imply removing ions from the compact layer. This prevents the surface from approaching further, hindering coagulation. This force is particularly relevant for systems with a thick Stern layer, i.e., when the counterions are large or heavily solvated. If the medium is water, the Stern layer repulsion can be coupled to the very strong repulsive hydration forces observed between hydrophilic surfaces, especially if multivalent, heavily hydrated, counterions are present.

Another consequence of the ion size is that ions with the same valence can have different effects on the interaction between surfaces, in contrast to the predictions of the PB equation, where identical valences lead to identical interactions. Extensions of the DLVO theory have been proposed to deal with the effect of ion size (see, e.g., [20]).

Concerning ion-ion interactions across the midplane, Guldbrand et al. [21] have shown that ion-ion correlations (ignored by the PB equation) can lead to attractive forces between equally charged surfaces, particularly if the counterions in the gap are multivalent and are confined into a small space. The strength of the attraction can overcome the osmotic repulsion, resulting in a net attractive interaction. Several approaches have been put forward to qualitatively and quantitatively describe this attraction, including modification of the PB equation to account for ion-ion interactions across the midplane [10, 22].

## Other non-DLVO interactions

Since most of the above-described shortcomings of the PB equation are apparent only at very small separations, the DLVO theory can in general predict the behavior of colloidal dispersion very accurately. It is, however, important to keep in mind that deviations from the expected behavior can occur. Not only the effects of the solvent, ion size and ion correlation should be considered, but also other forces



**Attractive force**
The concentration of polymer in the gap between two surfaces is zero at small separations. The liquid medium leaves the gap, resulting in an attractive force between the surfaces.

**Repulsive force**
Polymer chains are adsorbed or grafted to the particle surface
If two particles come close together:
- The configurational entropy of the polymers decreases
- The water concentration between the particles decreases

Both effects lead to a repulsive force!

**Attractive**
A single polymer chain adsorbs onto several particles simultaneously. A very deep secondary minimum appears.

**Fig. 17** Summary of the main surface forces induced by polymers in solution and/or adsorbed onto the surfaces not described by the DLVO theory (referred to as non-DLVO forces and interactions) can play an important role when describing the colloidal stability of a given system. Some relevant examples of these interactions are very briefly described in this section.

The presence of polymers in solution, for example, can result in an attractive depletion force between surfaces [23]. If the separation between the surfaces is small enough that the polymer chains do not fit in the gap (i.e., if the gap is depleted of polymer), a concentration gradient will appear. The dispersion medium will thus flow out of the gap driven by this gradient, resulting in an attractive force between the surfaces and leading to depletion flocculation (Fig. 17, left). The interaction minimum caused by depletion forces is however usually rather shallow; thus, colloidal particles flocculated by depletion forces can easily be re-dispersed. Depletion flocculation is thus widely used with the purpose of separating the particles from the medium with the objective of resuspending them again in another medium. An example is the separation and transfer of dispersed cells from one medium to another [24].

Adsorbed polymers, on the other hand, can lead to either a repulsive steric force (Fig. 17, center) or an attractive bridging force (Fig. 17, right) depending on the degree of surface coverage and the nature of the polymer [25]. Two surfaces coated by polymer will repel each other when the polymer chains on each surface overlap, as overlapping polymer chains have a reduced configurational entropy. Furthermore, the formation of a volume between the surfaces where the polymer concentration is very high results in an osmotic force driving the surfaces apart. Steric stabilization is widely used, for example, in pharmaceutical applications, where drug nanocarriers are usually coated by a grafted polymer layer (often polyethyleneglycol, PEG) to increase their circulation lifetime [26].

If the surface coverage of the polymers is low, however, a single polymer chain may adsorb onto several particles. Separating the particles from each other would mean stretching the polymer, thus decreasing its configurational entropy. Thus, a very strong attractive bridging force appears. In a colloidal dispersion, this force results in bridging flocculation [27]. The secondary minimum caused by bridging forces is very deep, so the aggregation is almost irreversible. Bridging flocculation is widely used, for example, in water treatment, to remove suspended particles [28].

Repulsive forces due to thermal fluctuations in soft particles play an important role in the stability of, e.g., liposomal dispersions and emulsions. The surface of a liposome, for example, will present different kinds of thermal fluctuations, such as wave formations (undulations), arising from the thermal motion of the molecules on the particle surface [29]. These fluctuations result in a repulsion between surfaces, since approaching each other would result in a decrease in the amplitude of the fluctuations (and thus their entropy). The fact that liposomes composed of zwitterionic lipids (i.e., with a zero surface charge density) remain dispersed over very long periods can be explained by these interactions.

Attractive forces due to (as yet not completely understood) long-range hydrophobic interactions are of great importance to understand the poor colloidal stability of hydrophobic particles dispersed in water. Two hydrophobic surfaces have been shown to attract each other even at separations > 100 nm [30]. How this attraction arises is not yet completely understood and an active field of research (e.g., [31]). Vapor bridging and/or water depletion near the surfaces are some of the proposed explanations for this phenomenon.

## Conclusions

The presented description of the DLVO theory and brief summary of other forces that may act between surfaces highlight the most important factors playing a role when describing the interaction between surfaces and, by extension, the stability of colloidal systems. Increasing the colloidal stability of a system means increasing the net repulsion between the particles, and this can be achieved by increasing their surface charge density or taking advantage of non-DLVO phenomena, such as steric stabilization. Decreasing the colloidal stability means, on the other hand, decreasing the repulsion or increasing the attraction between particles, and this can be achieved by increasing the ionic strength of the solution, decreasing the surface charge density of the particles, or with the help of non-DLVO effects, such as adding polymers to cause either depletion or bridging flocculation.

The forces described here are also relevant for the formation of liquid crystalline surfactant phases, foams, soap bubbles, etc. It is up to the curiosity and interest of the reader to explore the wide applications and possibilities of the PB equation and the DLVO theory, complemented in many cases with other non-DLVO interactions.

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## Declarations

**Conflict of interest** The author declares no competing interests.

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