

# 1 Introduction to colloid science and rheology

The subject of this book is the rheology of colloidal and nanoparticle dispersions. The reader will quickly appreciate the breadth of the subject area and, furthermore, that mastering colloidal suspension rheology requires some basic knowledge in colloid science as well as rheology. Thus, this chapter introduces some basic and simplified concepts in colloid science and rheology prior to embarking on the main theme of the book. As the term *colloid* is very general we necessarily need to focus on fundamental aspects of basic colloidal particles, their interactions, and their dispersion thermodynamic properties. These are, of course, the basis for understanding more complex systems. The rheology section is provided as an introduction to the basic concepts (a more advanced treatment of rheological testing of colloidal dispersions is provided in Chapter 9). Therefore, this chapter provides the minimum level of understanding that the reader will find valuable for understanding colloidal suspension rheology, as well as a means to introduce nomenclature and concepts used throughout the book. As a consequence, a reader familiar with either or both subjects may still find it valuable to skim through the material or refer back to it as needed.

## 1.1 Colloidal phenomena

Colloid science is a rich field with an equally rich literature. The reader is referred to a number of excellent monographs that cover the basics of colloid science in much greater detail. These will be presented without derivation. In particular, we use nomenclature and presentation of many ideas following *Colloidal Dispersions* [1] and *Principles of Colloid and Surface Chemistry* [2], which may be of help for further reading and inquiry, and for derivations of the results presented herein. Indeed, there are many additional excellent textbooks and monographs on colloid science, and references are provided where they are most relevant throughout this chapter as well as in the other chapters.

*Colloid* generally refers to the dispersed phase of a two-component system in which the elements of the dispersed phase are too small to be easily observed by an optical microscope and whose motion is affected by thermal forces. When the continuous phase, the *suspending medium*, is liquid they do not readily sediment and cannot pass through a membrane (such as in dialysis). Colloids appear in gels,

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emulsions, foods, biological systems, and coatings. Specific examples of colloids include milk, ink, paints, blood, and mayonnaise. They can be liquid or solid [1] particles dispersed in a gaseous, liquid, or solid medium, as well as gases dispersed in liquids and solids. When solid or liquid particles are dispersed in a gas they are known as aerosols, smoke, or fog. Association colloids are typically micelles formed from surfactants or block copolymers.

Colloids in a suspending medium are a type of mixture. Note that we use the term *dispersions*, as the term *suspension* often refers to mixtures where the dispersed phase particles are greater than colloidal in size. Chapter 2 discusses the rheology of non-colloidal particle suspensions. *Solutions*, at the other extreme, refer to molecular mixtures – although polymer and protein solutions are often treated, in many respects, effectively as colloidal dispersions. The reader will encounter terms such as colloidal dispersion, suspension, and solution used interchangeably in the literature.

Colloids occur naturally, and Robert Brown's original study of colloidal motion was carried out on pollen and spores. An early example of man-made colloidal dispersions is cited by Hunter as mixtures of lamp black and natural polymer used as inks by the ancient Egyptians and Chinese [3]. Another famous early example of the use of colloids is the Roman *Lycurgus cup*, dating from the fourth century AD, now in the British Museum [4]. Colloidal gold and silver in the glass comprising the cup leads to dichroic glass that is green upon observation but red when viewed with a light source inside. Medieval stained glass produces brilliant colors via suspended colloidal gold of varying size in the glass. Alchemists were familiar with the production of colloidal gold, which enabled gold to be dissolved and plated out onto surfaces by adsorption of gold colloids. Michael Faraday reported studies of the optical properties of solutions of gelatin-coated colloidal gold in his famous Bakerian Lecture in 1857. As will be discussed in more detail, colloids also played a seminal role in establishing the atomic theory of matter in the early twentieth century.

The definition given above, although vague, suggests a size range from  $\sim$ nm ( $10^{-9}$  m) to  $\sim$  $\mu$ m ( $10^{-6}$  m). The smaller size limit is required so that the mass of the colloid is significantly larger than the mass of the molecules comprising the suspending fluid. This is critical so that the suspending medium can be considered a continuum (i.e., characterized by continuum properties such as viscosity, dielectric constant, refractive index, etc.) on the time scale and length scale of colloidal motion. In part, we define a “colloid” by consideration of the forces acting on a “particle.” The upper size limit ensures that thermal forces are still significant in determining the motion of the colloidal particle and that gravitational settling does not simply remove particles from the dispersion.

### 1.1.1 Forces acting on individual colloids

The fundamental unit of energy in the colloidal and molecular world is the thermal energy  $k_B T$ , where  $k_B$  is Boltzmann's constant ( $1.381 \times 10^{-23}$  J K $^{-1}$ ) and  $T$  is the absolute temperature (K). Boltzmann's constant is also equal to  $R/N_A$  ( $R$ : gas constant,  $N_A$ : Avogadro's number). For reference, the translational energy of an ideal gas of hard spheres is  $(3/2)k_B T$  per particle. At 298 K, the energy  $k_B T$  is  $4.1 \times 10^{-21}$

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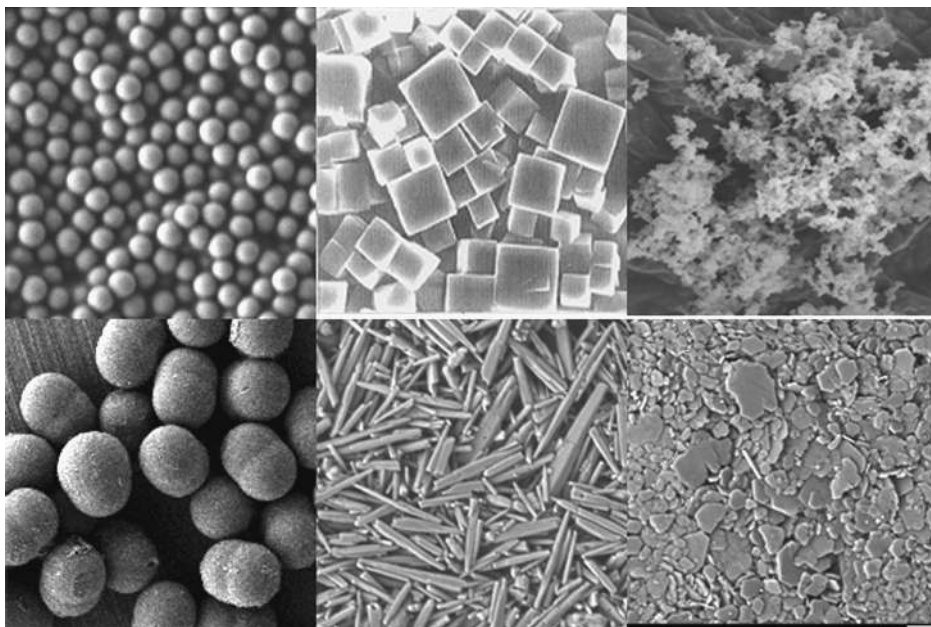


Figure 1.1. Some typical colloidal particles. Clockwise from upper left: silica spheres, lead sulfite crystals, fumed silica aerogel, polymer dumbbells, calcium carbonate rods, and kaolin clay. (Images courtesy of Dr. Ronald Egres, Dr. Caroline Nam, and Mark Pancyzk.)

J ( $\sim 4$  zeptojoules). Although this energy appears to be small, it sets the energy scale for all colloidal interactions. One important consequence of the motion resulting from thermal energy is the osmotic pressure arising from the presence of colloids (or polymers or salt ions, for that matter). For an ideal gas the thermal motion of the atoms leads to a pressure  $P = nk_B T$ , where  $n$  is the number density of the atoms. By analogy, the thermal motion of the colloid leads to an osmotic pressure  $\Pi$  in a colloidal dispersion, which for dilute systems leads to the van't Hoff law,

$$\Pi = nk_B T. \quad (1.1)$$

In 1851 George Stokes derived the frictional force acting on a sphere of radius  $a$  moving with velocity  $V$  immersed in a fluid of constant viscosity  $\eta_m$ . The symbol  $\eta_m$  is used throughout as the viscosity of the suspending medium, which is denoted  $\mu$  in many texts. The *hydrodynamic force* acting on a particle is also known as *Stokes drag*:

$$F^h = 6\pi\eta_m a V. \quad (1.2)$$

For water ( $\eta_m \approx 10^{-3}$  Pa s) the drag force on a particle with a radius of  $1 \mu\text{m}$  ( $10^{-6}$  m) and moving at a velocity  $V$  of  $1 \mu\text{m s}^{-1}$  ( $10^{-6}$  m s $^{-1}$ ) yields a characteristic drag force of  $\sim 2 \times 10^{-15}$  N, or  $\sim 2$  fN (femtonewtons).

The characteristic Brownian force acting on a colloidal particle is defined in terms of the thermal energy as

$$F^B = k_B T/a. \quad (1.3)$$

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For a 1  $\mu\text{m}$  particle, this force is on the order of  $4 \times 10^{-15}$  N, or  $\sim 4$  fN. The Brownian force arises from the random thermal collisions of the suspending medium molecules with the colloidal particles and leads to diffusive motion. It is named for the nineteenth-century botanist Robert Brown, who reported the phenomenon in 1827.

The theory of Brownian motion was elucidated independently by Albert Einstein (1905) [5] and by Marian von Smoluchowski (1906) [6]. The central result is an equation that relates the mean square displacement  $\langle (\Delta r)^2 \rangle$  of the colloidal particle, where  $r(t)$  is the distance a particle has diffused, by the time  $t$  allowed for diffusion:

$$\lim_{t \rightarrow \infty} \langle (\Delta r(t))^2 \rangle = 6Dt. \quad (1.4)$$

The coefficient  $\mathcal{D}$  is the Einstein-Smoluchowski diffusivity. It was calculated by Einstein and independently by William Sutherland, an Australian scientist, in 1905 [7]. For a spherical colloid,

$$\mathcal{D}_0 = k_B T / 6\pi\eta_m a. \quad (1.5)$$

This equation is known as the Stokes-Einstein-Sutherland equation. Einstein's work on the subject was motivated by the desire to determine molecular properties, specifically what we now call Avogadro's number,  $N_A$ . Validation of this prediction by Jean Perrin [8] led to one of three independent measures of  $N_A$ , which was critical as proof of the atomic theory of matter (see the framed story, *Colloids and the 1926 Nobel Prize for Physics*, in this chapter).

#### Colloids and the 1926 Nobel Prize for Physics

This is one of three Nobel Prizes directly attributed to investigations of colloidal phenomena – the others were awarded to R. A. Zsigmondy (1925) for the ultramicroscope and T. Svedberg (1926) for ultracentrifugation, both in chemistry. Einstein's work on Brownian motion was motivated in large part by a desire to prove the existence of atoms. Of central importance was the calculation of Avogadro's number, the number of atoms in a mole. The French physicist Jean Perrin investigated Brownian motion and applied the work of Einstein and von Smoluchowski to back-calculate Avogadro's number from his experiments.

It is very remarkable that these so familiar ideas become false on the scale of the observations which we can make under a microscope: each microscopic particle placed in water (or any other liquid), instead of falling in a regular manner exhibits a continuous and perfectly irregular agitation. It goes to and fro whilst turning about, it rises, falls, rises again, without tending in any way towards repose, and maintaining indefinitely the same mean state of agitation. This phenomenon which was predicted by Lucretius, suspected by Buffon, and established with certainty by Brown, constitutes the Brownian movement.

(from Perrin's Nobel Lecture <http://nobelprize.org>)

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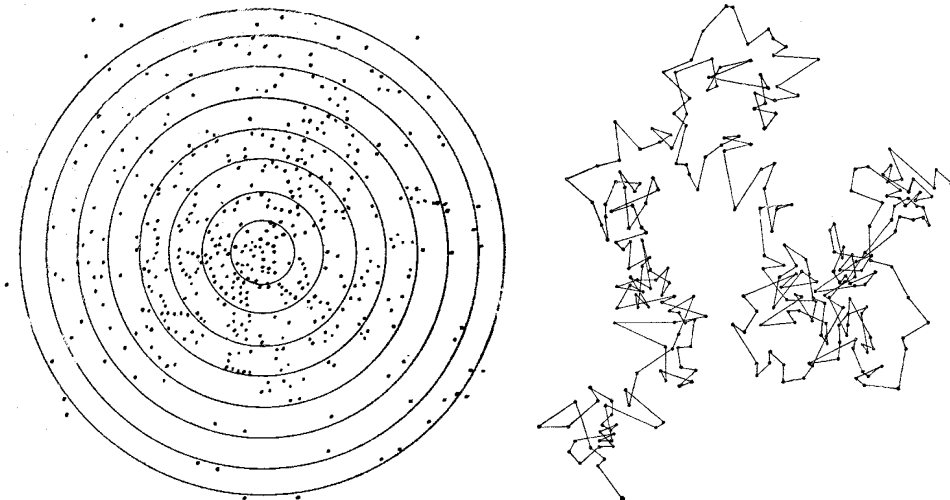


Figure 1.2. Jean Perrin's data, showing the location of colloidal particles released from the center at time zero and measured at time  $t$ . The right figure shows a typical trajectory of a  $0.53\ \mu\text{m}$  particle. (Used with permission from [9].)

Perrin used the fact that  $k_B = R/N_A$ , and that the gas constant  $R$  was known to great precision from the study of gases. Direct measurements of the displacement of colloids of known size in a fluid of known viscosity yielded  $\mathcal{D}$ , from the Einstein-Smoluchowski equation. The measurements are shown in Figure 1.2 [9].

From the indicated radial bins, Perrin calculated the mean square displacement at this time and, repeating the procedure for various times, particle sizes, and suspending fluids, obtained a value for Avogadro's number of  $6.4 \times 10^{23}$  (remarkably close to the accepted value of  $6.022 \times 10^{23}$ ). Interestingly, Perrin also used Einstein's predictions for rotational Brownian motion, measured using particles with small internal flaws so the rotational displacement could be measured. This yielded a value of  $6.5 \times 10^{23}$ . These measurements, along with two other methods for determining  $N_A$ , proved conclusively the atomic theory of matter.

The Brownian force also leads to a characteristic stress, which is typically scaled on the thermal energy per characteristic volume of the particle,  $\sim k_B T/a^3$ . Values for the colloidal size range are given in Table 1.1. This characteristic stress sets the scale for the elastic modulus of colloidal dispersions (see Chapter 3). The table illustrates the substantial reduction in characteristic stress that results from increasing particle size, which will have important consequences for the elastic moduli of colloidal gels and glasses.

Colloidal particles are subject to gravity; when the force of gravity is larger than the characteristic Brownian force, the particles will settle (or cream, if they are less dense than the suspending medium). The force of gravity  $F^g$  acting on a suspended spherical colloidal particle of density  $\rho_p$  in a suspending medium of density  $\rho_m$  is given by Archimedes' principle,

$$F^g = \Delta\rho V_p g = (\rho_p - \rho_m) \frac{4}{3} \pi a^3 g. \quad (1.6)$$

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Table 1.1. Specific surface area and characteristic stress for spherical particles of a given radius and a density of  $1000 \text{ kg m}^{-3}$ .

Radius (m)	Specific surface area ( $\text{m}^2 \text{g}^{-1}$ )	Characteristic stress (Pa)
$10^{-9}$	$1.50 \times 10^3$	$4.10 \times 10^6$
$10^{-8}$	$1.50 \times 10^2$	$4.10 \times 10^3$
$10^{-7}$	$1.50 \times 10^1$	$4.10 \times 10^0$
$10^{-6}$	$1.50 \times 10^0$	$4.10 \times 10^{-3}$

A typical gravitational force for a particle with a density  $100 \text{ kg m}^{-3}$  greater than that of the surrounding medium and a radius of  $1 \mu\text{m}$  is  $F^g \sim 4 \times 10^{-15} \text{ N}$ , or  $\sim 4 \text{ fN}$ . Thus, for colloidal-sized particles, the gravitational force is often comparable to or less than that of Brownian motion.

The Brownian force and gravity constitute the most common body forces acting on colloidal particles. Electrical and magnetic fields can also couple to the particles and can lead, interestingly, to particle chaining and *electro-* or *magneto-rheological* effects. Discussion of these forces can be found in Chapter 11.

### 1.1.2 Colloidal interactions

Two or more particles interact via dispersion, surface, depletion, and hydrodynamic forces, the difference being the source of the interactions. Hydrodynamic interactions arise from a disturbance induced in the fluid flow field by the presence of a particle, which in turn exerts a force on other particles within the range of the flow field. These interactions are discussed in Chapter 2. Dispersion forces arise from the ubiquitous quantum mechanical effects caused by fluctuations in the electron clouds surrounding atoms. Surface forces arise from the proximity of colloidal surfaces in a colloidal dispersion, where the surfaces can be charged, have adsorbed ions, nanoparticles, surfactants, or polymers, or may be covered with surface-grafted polymers. These forces can act to stabilize or destabilize colloids when the colloidal particles approach to within the range of the interaction. Depletion forces arise from soluble polymers or nanoparticles that lead to attractions when they are unable to access the space between particles in close proximity. Given a potential of interaction  $\Phi(r)$  that is a function of the separation  $r$  between particle centers, the force can be calculated as the derivative of the potential:

$$F(r) = -\frac{d\Phi(r)}{dr}. \quad (1.7)$$

Atoms and molecules interact by so-called dispersion forces, which in the simplified Drude model are a consequence of the polarization of the electron cloud of one atom by the fluctuating electron cloud of another. This fluctuation polarization leads, under most circumstances, to an attractive force between the atoms. Colloidal particles are subject to similar effects, whereby the atoms of one colloid induce polarization in the atoms of another. The net effect of this fluctuating polarization



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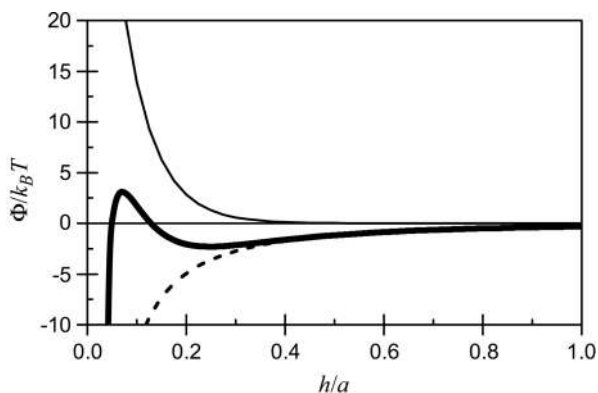


Figure 1.3. Interaction (DLVO) potential for 100 nm radius colloid particles with a surface charge of 25 mV and Hamaker constant of  $10 k_B T$  at a salt concentration of 50 mM. The solid line is the total potential, composed of the dispersion potential (Eq. (1.9), dashed line) plus the electrostatic potential (Eq. (1.12), thin line).

is known as the London-van der Waals or dispersion force between the particles. In its simplest manifestations, such as the force between two homogeneous plates in close approach, the dispersion interaction potential (per area of plate) has the simple form

$$\frac{\Phi^d(h)}{\text{area}} = -\frac{A}{12\pi h^2}, \quad (1.8)$$

where  $h$  is the distance between the particle surfaces. The coefficient  $A$ , known as the Hamaker constant, is a function of the material of the particles as well as that of the suspending medium (and, in the full theory, can also depend on the separation distance).  $A$  ranges from about  $30 \times 10^{-20}$  J, for gold particles in water, to values of the order of  $1 \times 10^{-20}$  J or less, for inorganic and polymeric particles (see p. xxi).

The dispersion potential is predicted to go to minus infinity as the surfaces touch. This suggests cold-welding of the particles and, indeed, the Hamaker constant can be estimated from the work of adhesion. For any real particle system, however, surface roughness, adsorbed or chemically bound ions, or solvent molecules on the surface will play a role in particle aggregation.

For two spherical colloidal particles with radii  $a_1$  and  $a_2$ , the potential is

$$\Phi^d(r) = -\frac{A}{6} \left( \frac{2a_1 a_2}{r^2 - (a_1 + a_2)^2} + \frac{2a_1 a_2}{r^2 - (a_1 - a_2)^2} + \ln \frac{r^2 - (a_1 + a_2)^2}{r^2 - (a_1 - a_2)^2} \right). \quad (1.9)$$

Figure 1.3 shows a plot of the dispersion potential from Eq. (1.9).

For 100 nm radius particles with  $A = 10^{-20}$  J (close to that for silica in water), Eq. (1.9) suggests that a surface layer of  $\sim 1$  nm will lead to a potential at contact of the order of  $-10^{-17}$  J ( $\sim -10^4 k_B T$ ), which is substantially larger than the Brownian or thermal energy. Dispersion forces between colloids act over a relatively long range, but become less than thermal forces for separations on the order of the particle size. In the absence of a stabilizing force, the particles will simply aggregate and settle out (or cream out) of solution. Therefore, colloidal dispersions must have some explicit means to impart colloidal stability. Such stability is often imparted via surface charge.

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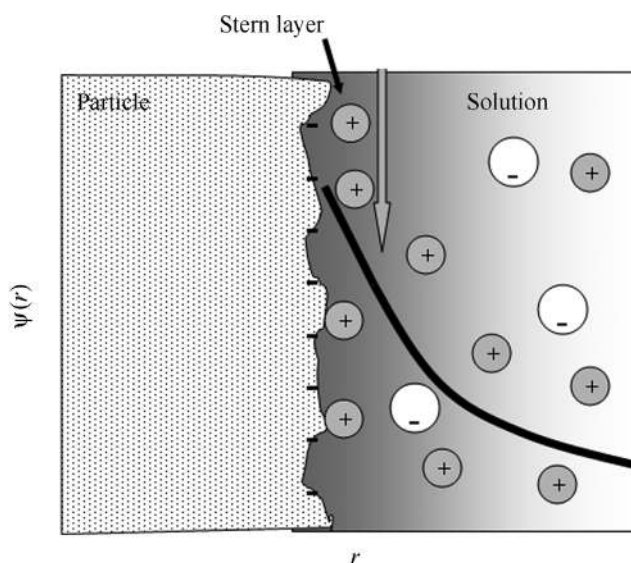


Figure 1.4. Schematic of a double layer in solution at the surface of a colloidal particle. The Stern layer is indicated, as well as the electrostatic potential  $\psi(r)$  (thick line). The potential at the Stern layer is often taken to be the  $\zeta$  potential.

Colloidal particles, by virtue of their small size, have a very large specific surface area. Table 1.1 illustrates the strong effect of particle size on specific surface area. Note that 1 g of nanometer-sized particles has a nominal surface area comparable to that of a football field. Not only is this highly relevant for adsorption, but it suggests that surface effects are extremely critical in colloidal dispersions.

Suspending particles in a liquid leads to charging of the surface, by either surface acids or bases (such as carboxylic, silane, or sulfate groups), by adsorption of free ions, as is typical in clays, or by adsorption of surfactants or polyelectrolytes. Thus, unless special precautions are taken, colloidal particles generally carry an electrical charge. The presence of dissociated chemical groups on the surface, of adsorbed ions, and of free counterions and added salt ions leads to a complex, structured electrostatic layer in solution near the particle surface.

Figure 1.4 depicts a simplified *double layer* of counterions (positively charged) surrounding a surface with negative charges (presumably due to dissociated acid groups, such as carboxyl or sulfate groups on polymer surfaces or  $\text{Si-O}^-$  groups for silica). The innermost layer of ions is adsorbed to the surface and the system is electroneutral, so the rest of the counterions are in solution. The shading denotes the density of these counterions. There are also cations and anions in solution arising from any additional, added electrolytes, such as salt (NaCl) or buffers.

The thick line in Figure 1.4 represents the electrostatic potential  $\psi(r)$  corresponding to this distribution of ions, which is calculated as a solution of the Poisson-Boltzmann equation (e.g., see [1, 2]). The ions in the Stern layer are considered to be immobile and this region acts as a capacitor over which the potential decays linearly. The outer limit of this region is associated with the plane of shear, beyond



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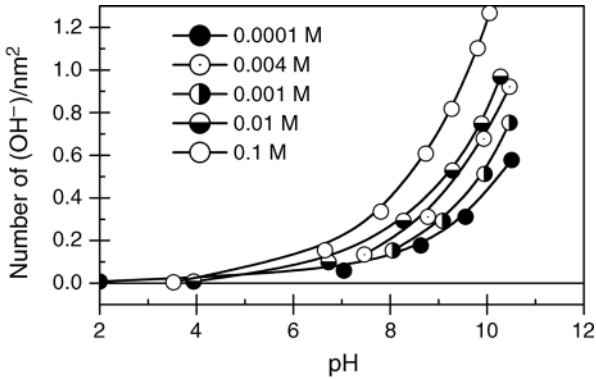


Figure 1.5 Surface charge (as number of OH<sup>-</sup> groups per nm<sup>2</sup>) for silica (Ludox) in water, showing the effect of pH and added electrolyte (NaCl, Molar). (After Iler [10].)

which the liquid around a moving particle is no longer trapped to move with the particle. The potential at this point is often taken to be the zeta ( $\zeta$ ) potential, determined by electrophoretic mobility measurements.

Beyond the Stern layer, the potential  $\psi(r)$  decays rapidly with a decay constant known as the Debye length,  $\kappa^{-1}$ . This length scale is determined by the ionic strength of the solution and the dielectric properties of the suspending medium as

$$\kappa^{-1} = \sqrt{\frac{\epsilon k_B T}{e^2 \left( \sum_i z_i^2 n_{i,\infty} \right)}} \tag{1.10}$$

For water at room temperature and for a 1:1 electrolyte (such as NaCl),  $\kappa^{-1}(\text{nm}) \sim 3\sqrt{C_{\text{salt}}/0.01M}$ , where the salt concentration is molar. Thus, the electrostatic screening length is on the order of 3 nm for 0.01 M (10 mM) 1:1 salt solutions. This should be compared with the particle radius  $a$  to assess whether the range of the electrostatic interaction is large. The larger the dimensionless group  $\kappa a$ , the thinner the double layer.

Some brief comments about the effect of ion type on electrostatic interactions are of value. Equation (1.10) shows that the screening length depends on the square of the ion valence ( $z_i$ ) but only the first power of the solution concentration of ions ( $n_{i,\infty}$ ). Therefore, divalent ions, such as  $\text{Ca}^{2+}$ , are much more effective in screening the electrostatic potential around particles. Multivalent counterions are also much more readily adsorbed in the Stern layer and can even lead to charge reversal, as when using trivalent alumina ions to create cationic (positively) charged silica particles at low pH [10]. Finally, although the equation does not distinguish specific ions other than by their charge, the effects of ion size and hydration can affect the propensity to adsorb in the Stern layer.

As the surface charge may be due to chemical dissociation of an acid or basic group, pH plays a large role in determining the charge on a colloid. A typical titration curve for silica is shown in Figure 1.5. Upon addition of base (NaOH) the surface silanol groups  $\text{SiO}^-$ , which are dissociated at low pH, become protonated and reverse charge at higher pH. The pH at which this reversal occurs, known as the point of zero charge (PZC), is often associated with colloidal aggregation due to the loss of electrostatic stabilization (see Chapter 6). For low surface charge densities and

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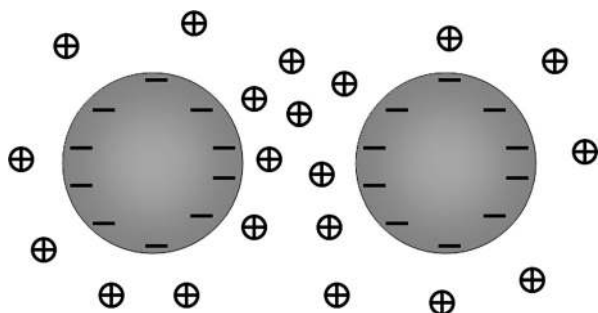


Figure 1.6. Two similar colloidal particles in solution, showing the associated ion distribution.

potentials, the surface charge  $Q$  on the particle is related to the surface potential  $\psi_s$  by

$$Q = 4\pi a \epsilon \epsilon_0 (1 + \kappa a) \psi_s. \quad (1.11)$$

The surface potential is often assumed to be the measured  $\zeta$  potential. The monograph by Hunter [3] provides a more detailed treatment of the possibilities and resulting electrostatic potentials surrounding various types of surfaces in a liquid.

Two colloidal particles interact when they approach closely enough that their respective electrostatic fields  $\psi(r)$  overlap, that is, when their surfaces are within a few multiples of the Debye screening length  $\kappa^{-1}$ . Each particle with its associated counterions is necessarily electroneutral. Therefore the colloidal interaction due to electrostatics is not simply electrostatic repulsion, as would be the case for charged spheres in a vacuum. In solution, the dominant contribution to the force acting between identical charged particles arises from the excess osmotic repulsion due to the excess number of ions in the surrounding double layer.

While the mathematical development of the total interaction potential  $\Phi^{el}$  arising from this complex situation is beyond the scope of this text, the physical principle leading to the repulsion between similar colloids can be deduced from the sketch in Figure 1.6. Specifically, the overlap of the double layers results in an increased ion concentration between the two particles. As a consequence, the local osmotic pressure is higher between the two particles, as shown in Eq. (1.1). This excess osmotic pressure acts to push the particles apart until the two double layers are separated. Under the assumptions that the two colloids have the same size and surface potential and that the electrostatic fields surrounding each particle can be linearly added, the following expression for the potential of interaction due to electrostatic interactions in the presence of a symmetric electrolyte of valence  $z$  results:

$$\Phi^{el}(h) = 32a\epsilon\epsilon_0 \left(\frac{kT}{ze}\right)^2 \tanh^2\left(\frac{\psi_s ez}{4k_B T}\right) \exp(-\kappa h). \quad (1.12)$$

where  $h = r - 2a$  is the surface-to-surface distance between the particles. Equation (1.12) shows that the interaction potential decays exponentially with the characteristic length given by the Debye screening length, as expected. The magnitude of the potential is determined by the surface potential, but also depends on the particle size,