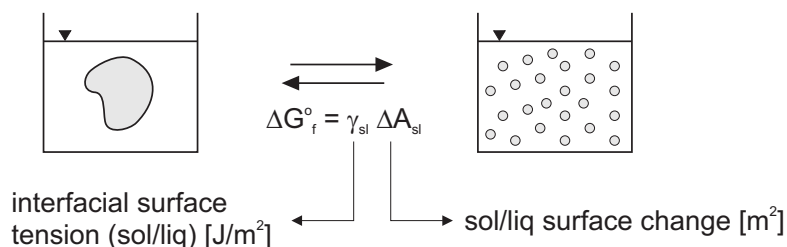


# Chapter 6

## Stability of Colloidal Suspensions

### 6.1 Kinetic Stability of Colloidal Suspensions



$\gamma_{sl} > 0 \Rightarrow$  colloid state is unstable, i.e., lyophobic (in water: hydrophobic); you need work to create a dispersion ( $\Rightarrow$  mixing)

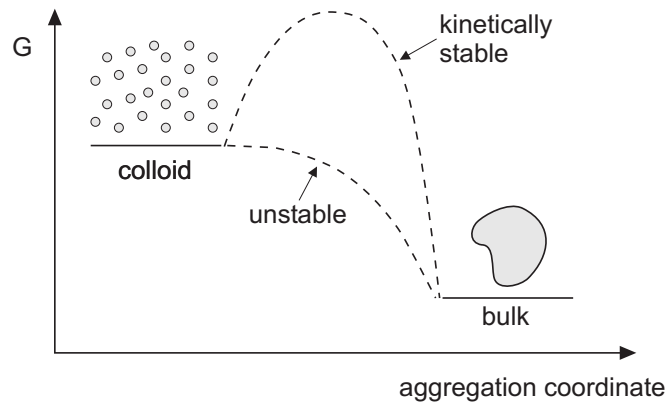
$\gamma_{sl} < 0 \Rightarrow$  colloid state is stable, i.e., lyophilic (in water: hydrophilic)

Lyophobic colloids can be made kinetically stable by building an energy barrier sufficiently large with respect to the thermal energy of the particles,  $kT$ . Two stabilization mechanisms are possible:

- electrostatic: the particles are electrically charged
- steric: the particles are coated with some material (e.g. polymer) which prevents their close approach.

#### Concept of Kinetic Stability

Thermal energy provides kinetic energy to the colloidal particles which collide with energy ( $kT$ ). The charges on the particle surface provide an energy barrier to be overcome in order to have aggregation.



## 6.2 Interaction between two Charged Bodies

The interaction between two bodies is dominated by two forces, an attractive van der Waals force and a repulsive electrostatic force.

### 6.2.1 van der Waals Forces

The origin of these forces is the attraction between a temporary dipole and the corresponding induced dipoles (London theory). The following semi-quantitative argument provides a reasonably accurate picture of the physics underlying these interactions. Let us use the Bohr model for a hydrogen atom, where electrons are regarded as traveling in well defined orbits around nuclei. As a result of the electrons motion, every atom has an instantaneous dipole moment  $p$  approximately equal to  $p = a_0 * e$ , where  $e$  is the electron charge and  $a_0$  is the Bohr radius, which is a good estimate of the radius of a hydrogen atom. Let us consider two hydrogen atoms, referred to as atom 1 and atom 2, positioned at a distance  $R$ . The electric field  $E$  generated by the instantaneous dipole 1 at distance  $R$  is given by:

$$E = \frac{p_1}{4\pi\epsilon_0 R^3} \quad (6.1)$$

where  $\epsilon_0$  is the vacuum dielectric permeability. Atom 2, will be polarized by the electric field generated by atom 1, which generates an induced dipole of strength:

$$p_2 = \alpha E = \frac{\alpha p_1}{4\pi\epsilon_0 R^3} \quad (6.2)$$

## CHAPTER 6. STABILITY OF COLLOIDAL SUSPENSIONS

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where  $\alpha$  is the polarizability of the second atom, and is approximately equal to  $\alpha = 4\pi\epsilon_0 a_0^3$ . Since the energy of interaction of two dipoles equals:

$$V_{\text{int}} = -\frac{p_1 p_2}{4\pi\epsilon_0 R^3} = -\frac{\alpha a_0^2 e^2}{(4\pi\epsilon_0)^2 R^6} = -\frac{C}{R^6} \quad (6.3)$$

Equation (6.3) shows that van der Waals interactions between pairs of particles in vacuum are always attractive, and decay very strongly with the distance. However, they become considerable at short distances.

When the overall van der Waals interactions between macroscopic objects needs to be computed, one assumes that equation (6.3) holds for all pairs of molecules contained in the two objects. This theory has been developed by Hamaker. In this case, the van der Waals interaction between macroscopic object 1 and macroscopic object 2 is given by:

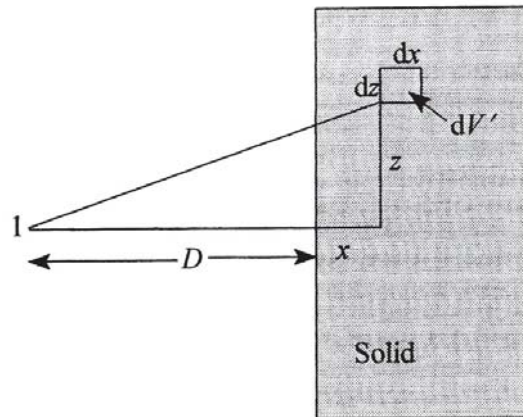
$$V_A = -C \int_{V_1} \int_{V_2} \frac{dV_1 dV_2}{R^6} \quad (6.4)$$

where the two integrations run over the entire volumes  $V_1$  and  $V_2$  of the two bodies, and  $R$  is the distance between two arbitrary points, one located within the first object, the other one within the second object. Generally, the two integrals are difficult to compute, and explicit formulas are available only for very simple geometries. As an example, let us perform the integration for the case of a semi-infinite solid and a point. Equation (6.4) reduces in this case to one single volume integral, over the semi-infinite body. If we indicate with  $d$  the distance between the point (named 1) and the surface of the semi-infinite body, and we define a coordinate system with the  $x$ -axis along the direction of the distance  $d$ , with the zero on the surface of the body and pointing inwards the body and both other axes parallel to its surface, one can immediately recognize that the system has a rotational symmetry around the  $x$ -axis. It is therefore convenient to perform the volume integration using cylindrical coordinates. The distance  $R$  in equation (6.4) is equal to the distance between point 1 and an arbitrary point having coordinates  $x$  and  $z$  inside the body, as shown in the next Figure. By making use of Pitagora's theorem, the volume integral in equation (6.4) reduces to:

$$V_A = -C \int_0^\infty dx \int_0^\infty \frac{2\pi z dz}{(z^2 + (d+x)^2)^3} = -\frac{\pi C}{2} \int_0^\infty \frac{dx}{(d+x)^4} = -\frac{\pi C}{6d^3} \quad (6.5)$$

From equation (6.5) one can observe that the dependence of the van der Waals interactions between a point and an infinite solid decreases as the reverse third power of the distance.

The simple calculation shows the effect of summing in a pair additive manner the interactions of all pairs of molecules belonging to two macroscopic objects. Even though the



interactions of two molecules are very weak, the overall interactions between the bodies can become significant at short distances, for example at distances comparable to the size of the two objects.

There are two important cases where the integrations in equation (6.4) can be performed analytically: (1) two infinite slabs and (2) two spheres having arbitrary size and distance. The corresponding interaction potentials can be computed as follows:

- For two infinite slabs at distance  $D$ :

$$V_A(D) = -\frac{A}{12\pi D^2} \quad (6.6)$$

- For two spheres of radius  $a_1$  and  $a_2$  at distance  $R$ :

$$V_A(R) = -\frac{A}{6} \left[ \frac{2a_1a_2}{R^2 - (a_1 + a_2)^2} + \frac{2a_1a_2}{R^2 - (a_1 - a_2)^2} + \ln \left( \frac{R^2 - (a_1 + a_2)^2}{R^2 - (a_1 - a_2)^2} \right) \right] \quad (6.7)$$

where  $A$  is the Hamaker constant which depends on the physical characteristics, e.g., polarizability and density, of the materials involved. In the case of two spheres, one can perform Taylor expansions of this last equation and observe that at distances much smaller than the particle radius, the interactions decay with the first power of the distance. On the other hand, for distances much larger than the particle radius the interaction energy decays with the sixth power of the distance, as one could expect.

The Hamaker constant depends not only on the physical properties of the materials the macroscopic objects are made of, but also on the dielectric properties of the medium surrounding the particles. The effect of this medium can be extremely important in some cases.

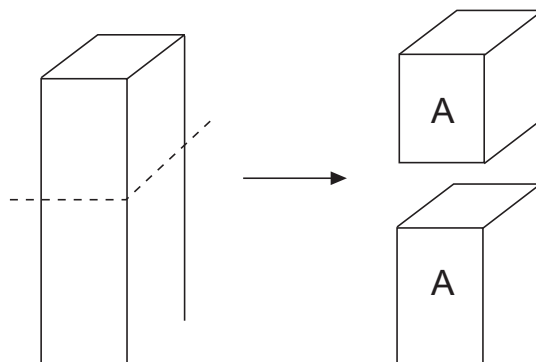
## CHAPTER 6. STABILITY OF COLLOIDAL SUSPENSIONS

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In fact, even though Hamaker constants are usually positive, there are some cases where negative values can be found for some specific types of materials/medium pairs. A negative value of Hamaker constant implies that van der Waals interactions are repulsive.

One final caveat about Hamaker's treatment of van der Waals interactions. A much more rigorous approach of dispersion forces and van der Waals forces is available in the literature, which has been pioneered by Lifshitz. It is based on rigorous quantum mechanical calculations, but the final equations are far more complex than the Hamaker theory. However, some general features can be quickly discussed, which are necessary to point out the limitations of the simpler Hamaker theory. First of all, Lifshitz' theory shows that the pairwise addition of interactions is not rigorously correct, as van der Waals interactions are a truly many-body problem. This effect can be simply accounted for by adjusting the values of the Hamaker constant. The second limitation is given by the so-called retardation effect. Since atoms are fluctuating dipoles, as the distance between two molecules increases beyond a certain threshold, the time required for a molecule to feel the effect of the electric field produced by another dipole becomes significant. This implies that the interactions of the different dipoles are retarded, and the energy of interaction decays even stronger with the distance, i.e., with the seventh power of the distance, and not anymore with the sixth power. This effect weakens van der Waals interactions for large bodies as their distance increases, compared to the predictions of the Hamaker theory. However, due to its simplicity and good accuracy, Hamaker constants are still commonly used in colloidal science.

### Concept of Surface Tension



$W_{AA}$  = work per unit area needed to separate up to  $\infty$  two parts of liquid column

## CHAPTER 6. STABILITY OF COLLOIDAL SUSPENSIONS

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$$W_{AA} = 2\gamma_{Av} \quad (6.8)$$

where  $\gamma_{Av}$  is the surface tension of  $A$  in contact with vapor (vacuum). We compute  $W_{AA}$  as the interaction energy between two flat bodies and get (for hydrocarbons):

$$\gamma_{Av} = \frac{1}{2}W_{AA} = \frac{1}{2} \cdot \frac{A}{12\pi L^2} \quad (6.9)$$

Since it is difficult to postulate  $L$ , we compute it from experimental values of  $\gamma_{Av}$  and calculated  $A$ .

Alkane  $C_nH_{2n+2}$

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$n$	$10^{20} \times A$ (J)	$10^3 \times \gamma_{Av}$ (J/m <sup>2</sup> )	$10^{-3} \times \rho$ (kg/m <sup>3</sup> )	$L$ (nm)
5	3.75	16.05	0.626	0.176
6	4.07	18.40	0.660	0.171
8	4.50	21.62	0.702	0.166
10	4.82	23.83	0.730	0.164
12	5.03	25.35	0.749	0.162
14	5.05	26.56	0.763	0.159
16	5.23	24.47	0.773	0.159

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We observe that  $L$ :

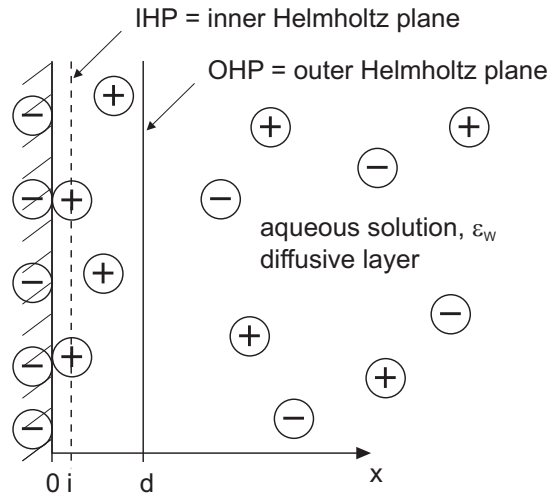
i) has dimension of molecular radius

ii)  $L \propto 1/\sqrt{\rho}$ .

### 6.2.2 Electrostatic Forces

#### Electrical Double Layer

- Outside of the outer Helmholtz plane, the ions move freely, therefore this is the plane of closest approach of (hydrated) ions ( $\approx 0.5$  nm).
- The inner Helmholtz plane constitutes the locus of the centers of adsorbed (dehydrated) ions ( $\approx 0.1$  nm).



For  $x > 0$ :

$$\left. \begin{aligned} \rho &= \text{div}(\epsilon E) \\ E &= -\text{grad}(\psi) \end{aligned} \right\} \Rightarrow \nabla^2(\psi) = -\frac{\rho}{\epsilon} \quad \left( \begin{array}{l} \text{Poisson} \\ \text{equation} \end{array} \right) \quad (6.10)$$

where  $\rho = \sum_{\text{all ions}} n_i z_i e$ , with  $n_i$  = number ion concentration,  $z_i$  = valance,  $e$  = electron charge;

$E$  = electric field

$\epsilon$  = permittivity

$\psi$  = potential referred to bulk, i.e.,  $\psi = 0$  at  $x = \infty$ .

For  $x > d$ :

The ions are free to diffuse and are influenced by the local electrostatic potential, so that:

$$n_i = n_i^0 \exp\left(-\frac{z_i e \psi}{kT}\right) \quad \left( \begin{array}{l} \text{Boltzmann} \\ \text{equation} \end{array} \right) \quad (6.11)$$

where  $n_i^0$  is  $n_i$  in the bulk. In the diffusive layer,  $x > d$ , we have  $\epsilon = \epsilon_w$  and:

$$\nabla^2(\psi) = -\frac{1}{\epsilon_w} \sum n_i^0 z_i e \exp\left(-\frac{z_i e \psi}{kT}\right) \quad \left( \begin{array}{l} \text{Poisson-Boltzmann} \\ \text{equation} \end{array} \right) \quad (6.12)$$

with B.C.:  $\psi = 0$  at  $x = \infty$ ,  $\psi = \psi_d$  at  $x = d$ .

Let us consider a few specific cases for which we have analytical solutions.

- The Debye-Hückel approximation:

Applies when the electrical energy is small compared to the thermal energy:  $|z_i e \psi| < kT$ .

Then,

$$\exp\left(-\frac{z_i e \psi}{kT}\right) \approx 1 - \frac{z_i e \psi}{kT} \quad (6.13)$$

which leads to

$$\nabla^2\psi = -\frac{1}{\varepsilon_w} \left( \sum n_i^0 z_i e - \frac{\sum n_i^0 z_i^2 e^2}{kT} \psi \right) \quad (6.14)$$

According to the principle of electroneutrality for the bulk  $\sum n_i^0 z_i = 0$  and, therefore, we get

$$\nabla^2\psi = \kappa^2\psi \quad (6.15)$$

where

$$\kappa^2 = \frac{1}{\varepsilon_w} \frac{\sum n_i^0 z_i^2 e^2}{kT} \quad (6.16)$$

is the Debye-Hückel parameter. The solution has the form

$$\psi = A_1 \exp(\kappa x) + A_2 \exp(-\kappa x) \quad (6.17)$$

but since  $\psi = 0$  as  $x \rightarrow \infty$ ,  $\Rightarrow A_1 = 0$  and imposing  $\psi = \psi_d$  at  $x = d \Rightarrow A_2 = \psi_d \exp(\kappa d)$ , so that

$$\psi = \psi_d \exp[-\kappa(x - d)] \quad , \text{ for } x > d \quad (6.18)$$

The distance  $1/\kappa$  where  $\psi = \psi_d \exp(-1)$  is defined as the thickness of the diffusive layer. At 25°C in water

$$\kappa = 3.29 \sqrt{I} \quad [\text{nm}^{-1}] \quad (6.19)$$

with  $I = 1/2 \sum c_i z_i^2$  is the ionic strength and  $c_i$  is in mol/L. For example, for a  $10^{-3}$  M, 1:1 electrolyte is  $1/\kappa = 9.6$  nm.

- Flat surface:

We consider a symmetric electrolyte,  $z_+ = -z_- = z$  and  $n_+^0 = n_-^0 = n^0$ , so that the Poisson-Boltzmann equation becomes

$$\begin{aligned} \nabla^2\psi &= -\frac{1}{\varepsilon_w} n^0 z e \exp\left(-\frac{ze\psi}{kT}\right) + \frac{1}{\varepsilon_w} n^0 z e \exp\left(+\frac{ze\psi}{kT}\right) \\ &= \frac{2n^0 z e}{\varepsilon_w} \sinh\left(\frac{ze\psi}{kT}\right) \end{aligned} \quad (6.20)$$

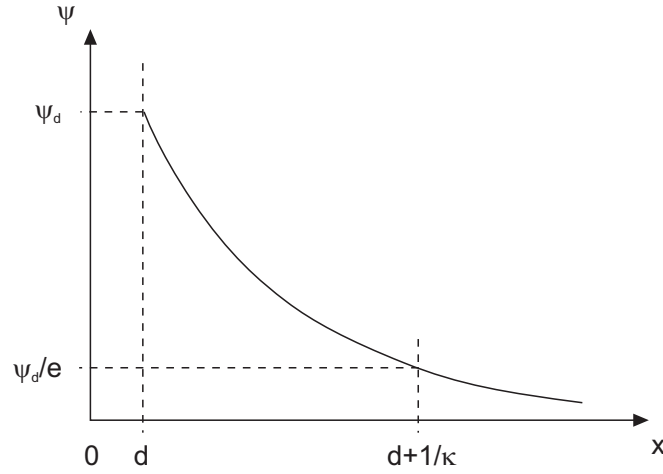
and then for a flat geometry

$$\frac{d^2\psi}{dx^2} = \frac{2n^0 z e}{\varepsilon_w} \sinh\left(\frac{ze\psi}{kT}\right) \quad (6.21)$$

Multiplying both sides by  $(2d\psi/dx)$  and integrating in  $x$ :

$$\int 2 \frac{d\psi}{dx} \frac{d^2\psi}{dx^2} dx = \frac{4n^0 z e}{\varepsilon_w} \int \sinh\left(\frac{ze\psi}{kT}\right) \frac{d\psi}{dx} dx \quad (6.22)$$





$$\int_{\infty}^x \frac{d}{dx} \left( \frac{d\psi}{dx} \right)^2 dx = \frac{4n^0 z e}{\epsilon_w} \int_0^{\psi} \sinh \left( \frac{ze\psi}{kT} \right) d\psi \quad (6.23)$$

where we account for the B.C.:  $\psi = 0$  and  $d\psi/dx = 0$  at  $x = \infty$

$$\left( \frac{d\psi}{dx} \right)^2 = \frac{4n^0 z e}{\epsilon_w} \left| \frac{kT}{ze} \cosh \left( \frac{ze\psi}{kT} \right) \right|_0^{\psi} \quad (6.24)$$

$$\left( \frac{d\psi}{dx} \right)^2 = \frac{4n^0 kT}{\epsilon_w} \left[ \cosh \left( \frac{ze\psi}{kT} \right) - 1 \right] \quad (6.25)$$

Recalling that  $\sqrt{\cosh(a\psi) - 1} = -\sqrt{2} \sinh(a\psi/2)$ , we get

$$\frac{d\psi}{dx} = - \left( \frac{8n^0 kT}{\epsilon_w} \right)^{\frac{1}{2}} \sinh \left( \frac{ze\psi}{2kT} \right) \quad (6.26)$$

This can be integrated by variable separation as follows:

$$\int_{\psi_d}^{\psi} \frac{d\psi}{\sinh(ze\psi/2kT)} = - \frac{2\kappa kT}{ze} \int_d^x dx \quad (6.27)$$

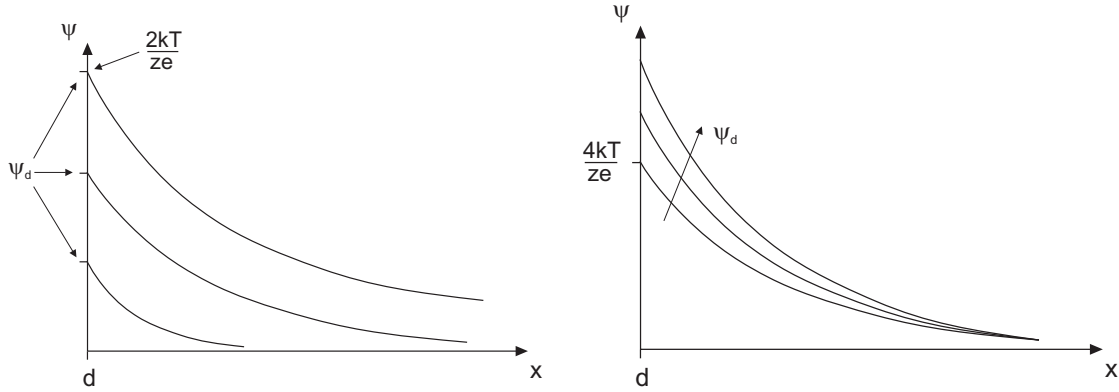
$$\Rightarrow \tanh \left( \frac{ze\psi}{4kT} \right) = \tanh \left( \frac{ze\psi_d}{4kT} \right) \exp[-\kappa(x-d)] \quad (6.28)$$

In the case where  $ze\psi < kT$ , we can approximate  $\tanh(ze\psi/4kT) \approx ze\psi/4kT$ , and the solution above becomes

$$\psi = \psi_d \exp[-\kappa(x-d)] \quad (6.29)$$

which is the Debye-Hückel approximate solution.

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a) Approximate behavior:

$$\text{for } \psi_d < 2 \frac{kT}{ze} \Rightarrow \psi \approx \psi_d \exp[-\kappa(x-d)]$$

$$\text{for } \psi_d > 4 \frac{kT}{ze} \Rightarrow \tanh\left(\frac{ze\psi}{4kT}\right) \approx \exp[-\kappa(x-d)]$$

(since  $\tanh(y) \rightarrow 1$  as  $y \rightarrow \infty$ )

which sufficiently away from the surface, where  $\psi$  is small, leads to

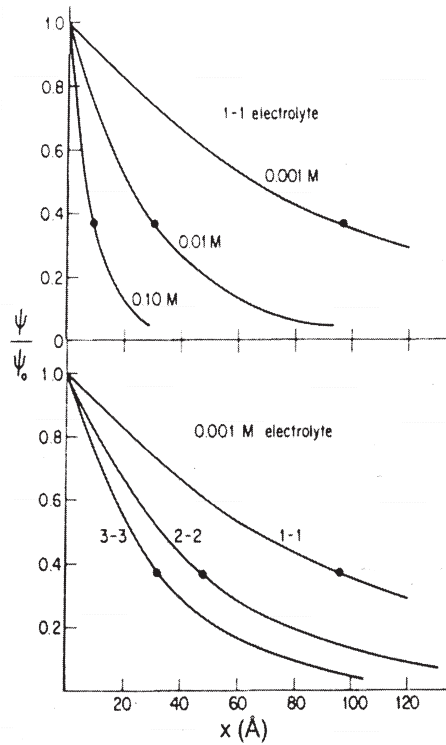
$$\psi = \frac{4kT}{ze} \exp[-\kappa(x-d)] \quad (6.30)$$

that is away from the surface the potential behaves like in the case where  $\psi_d = 4kT/ze$ , although  $\psi_d$  is much larger.

b) If we take  $d = 0$ , and ignore the IHP and OHP, this treatment corresponds to the Gouy and Chapman model. The figures show the effect of electrolyte charge and concentration on the potential behavior predicted by Debye-Hückel. The points indicate the value  $\psi/\psi_d = \exp(-1)$  and the corresponding Debye thickness  $1/\kappa$ .

$1/\kappa$	$C_{\text{electrolyte}}$
9.60 nm	0.001 M
3.00 nm	0.01 M
0.96 nm	0.1 M

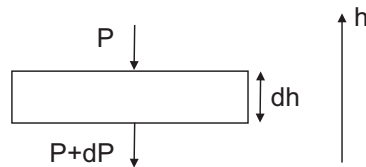
It is seen that both the electrolyte concentration and its charge can strongly affect the thickness of the double layer. This is known as double layer compression and is widely used in applications to destabilize colloids. However, the predictions of this model on a quantitative basis are often unrealistic. For example in the case of  $\psi_d = 100$  mV with



$n^0 = 0.001$  M, a surface concentration value  $n_d = n^0 \exp(ze\psi_d/kT) = 0.001 \exp(12) = 160$  M is obtained. This result can be corrected introducing the Stern layer, where some counterions are strongly associated with the surface, thus also neutralizing some of the surface ions.

**Simple Example for a Boltzmann Distribution**

Let us consider the molecules in the atmosphere which are free to move according to Brownian motion but are also subject to the gravitational field.



By applying Newton law to a thin slice of atmosphere  $dh$  we get:

$$dP = -\rho g dh \tag{6.31}$$

## CHAPTER 6. STABILITY OF COLLOIDAL SUSPENSIONS

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where  $\rho$  is the mass density which using the ideal gas law can be expressed as follows:

$$\rho = nM = \frac{PM}{RT} \quad (6.32)$$

where  $M$  is the molecular weight and  $n$  is the number molecule concentration. Substituting in the previous equation this leads to:

$$\frac{dP}{P} = -\frac{Mg}{RT} dh \quad (6.33)$$

which integrated with I.C.:  $P = P_0$  at  $h = 0$  yields:

$$P = P_0 \exp\left(-\frac{Mg}{RT}h\right) \quad (6.34)$$

Recalling that  $M = mN_A$ , where  $m$  is the molecule mass and  $N_A$  the Avogadro number, while  $R = kN_A$  and pressure is proportional to the number molecule concentration the above equation leads to:

$$n = n_0 \exp\left(-\frac{mgh}{kT}\right) \quad (6.35)$$

which, since  $(mgh)$  is the gravitational potential, coincides with the Boltzmann equation (6.6).

### A More Rigorous Derivation of the Boltzmann Distribution

In order to fully justify the use of the Boltzmann distribution to describe the dependence of the concentration of ions on the electrostatic potential, let us consider the following thermodynamic argument. In the presence of a charged surface, which generates an electric field, the thermodynamic function which determines the equilibrium condition of the ions is the electrochemical potential  $\tilde{\mu}$ , defined as:

$$\tilde{\mu} = \mu + ze\psi \quad (6.36)$$

where  $z$  is the valence of the ion,  $\psi$  is the electrostatic potential at the location considered and  $\mu$  is the chemical potential. The significance of the electrochemical potential is that of free energy per molecule in the presence of electric field. For every ion, the electrochemical potential has to be constant in the entire space in order to guarantee the thermodynamic equilibrium. Therefore, by considering two different locations, one at distance  $x$  from the surface, where the electrostatic potential is  $\psi(x)$ , and the other one in the bulk of the solution, at infinite distance from the surface, where the electrostatic potential is equal to zero, the equilibrium conditions reads:

$$\tilde{\mu}(x) = \mu(x) + ze\psi(x) = \tilde{\mu}(x = \infty) = \mu(x = \infty) \quad (6.37)$$

## CHAPTER 6. STABILITY OF COLLOIDAL SUSPENSIONS

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By using the definition of chemical potential:

$$\mu(x) = \mu_0 + kT \ln(a(x)) \quad (6.38)$$

where  $a(x)$  is the activity of the species at a distance  $x$  from the surface and  $\mu_0$  is a reference chemical potential. By neglecting concentration effects, we can replace the activity by the number concentration, i.e.,  $a(x) \approx n(x)$ . Therefore, by calling  $n_0$  the number concentration of the ion in the bulk of the solution, equation (6.37) becomes:

$$kT \ln(n(x)) + ze\psi = kT \ln(n_0) \quad (6.39)$$

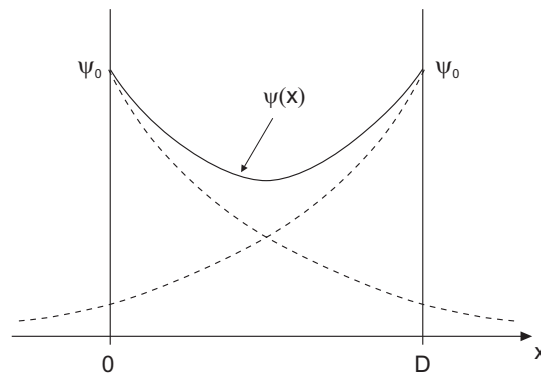
which leads to the Boltzmann distribution of the ion:

$$n(x) = n_0 \exp\left(-\frac{ze\psi}{kT}\right) \quad (6.40)$$

Therefore, the Boltzmann distribution arises naturally (at least for dilute electrolyte solutions) as a consequence of thermodynamic equilibrium in the presence of an electric field.

### Electrostatic Potential of Interaction

When two charged bodies approach each other the corresponding double layers overlap, the local ion concentration increases compared to the bulk, thus creating an osmotic pressure and therefore a corresponding repulsive force.



Depending on the kinetics of the approach we can have that the ions may have or not time enough to equilibrate. We distinguish three limiting situations:

- constant surface potential,  $\psi_0 \Rightarrow$  slow approach;

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**CHAPTER 6. STABILITY OF COLLOIDAL SUSPENSIONS**

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- constant surface charge,  $\sigma_0 \Rightarrow$  fast approach or ions covalently bound to the surface;
- charge regulation  $\Rightarrow$  the surface groups can dissociate to an extent which depends on the interaction, as for example:

$$\text{SH} \rightleftharpoons \text{S}^- + \text{H}^+ \Rightarrow \sigma_0 = -eS_s^- = \frac{-e\kappa_d N_s}{\kappa_d + \text{H}^{+0} \exp(-e\psi_0/kT)} \quad (6.41)$$

In order to compute the repulsive force between two charged infinite planar surfaces at a distance  $h$ , let us consider the following simple argument. At equilibrium, all forces acting on a volume element located between the two plates must balance. The only two forces acting are the electrostatic forces and the osmotic pressure. The osmotic pressure force per unit volume is equal to:

$$F_p = -\frac{dp}{dx} \quad (6.42)$$

where  $x$  is the coordinate perpendicular to the two surfaces. On the other hand, the electrostatic force per unit volume equals the product of the charge density with the electric field, and can be written as:

$$F_{\text{el}} = -\rho \frac{d\psi}{dx} \quad (6.43)$$

By using the Poisson equation, this force balance can be recast in the following form:

$$\frac{dp}{dx} - \epsilon \frac{d^2\psi}{dx^2} \frac{d\psi}{dx} = 0 \quad (6.44)$$

The integration of this equation gives:

$$p - \frac{\epsilon}{2} \left( \frac{d\psi}{dx} \right)^2 = \text{const.} \quad (6.45)$$

This last equation implies that the sum of the osmotic pressure and the so-called Maxwell pressure,  $\epsilon/2 \cdot (d\psi/dx)^2$ , are constant in the whole domain. Due to the symmetry of the system considered here, at the midplane the electrostatic potential profile has to have an extremum (minimum if the surface are positively charged, maximum otherwise). Therefore  $(d\psi/dx)_{x=h/2} = 0$ , and the constant in equation (6.45) is equal to the osmotic pressure at the midplane. Therefore, once the pressure at midplane is known, the force acting on the planes can be computed, and by integrating the force, the energy of interaction can be derived. In order to determine the pressure at midplane, we can once again use the force balance written as:

$$dp = -\rho d\psi \quad (6.46)$$

## CHAPTER 6. STABILITY OF COLLOIDAL SUSPENSIONS

In order to simplify the calculations, let us assume to have a solution containing just a symmetric  $z-z$  electrolyte. By making use of the Boltzmann distribution for the ions concentration, one obtains:

$$dp = 2zen_0 \sinh\left(-\frac{ze\psi}{kT}\right) d\psi \quad (6.47)$$

This equation can be easily integrated between the following limits:  $p = p_0$  in the bulk (when  $\psi = 0$ ), and  $p = p_{h/2}$  at  $\psi = \psi_{h/2}$ . The result is the following:

$$p_{h/2} - p_0 = 2kTn_0 \left[ \cosh\left(-\frac{ze\psi_{h/2}}{kT}\right) - 1 \right] = F_R \quad (6.48)$$

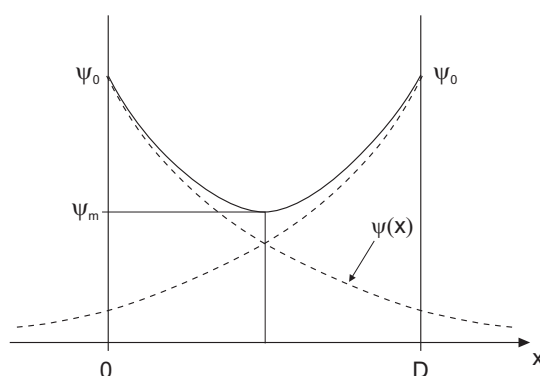
The conclusion is that the repulsive force between the planes can be computed if the potential at midplane is known. This can be obtained by integrating the Poisson-Boltzmann equation. One should then notice that the electrostatic repulsive energy (per unit surface) is obtained from the repulsive force per unit surface as follows:

$$dV_{el} = -F_R dh \quad (6.49)$$

The physical interpretation is that the potential energy per unit surface of two plates at a distance  $h$  is equal to minus the work done to bring the plates from infinite distance to the current distance  $h$ .

Several approximate relations have been developed to compute the electrostatic repulsive potentials between two bodies.

- For small degree of double layer overlap (any geometry),  $D \gg 1/\kappa$ :



$$V_R^\psi = \frac{64n^0kTZ^2}{\kappa} \exp(-\kappa D) \quad (6.50)$$

$$Z = \tanh\left(\frac{ze\psi_0}{4kT}\right) \quad (6.51)$$

In this case  $V_R^\sigma \approx V_R^\psi$  since the discharge remains anyway small due to the small overlap. This corresponds to the case where the potential at midplane is approximated by the sum of the potentials of two isolated charged infinite planes. This approximation is only valid for small overlapping.

- For small potentials of the two surfaces,  $ze\psi_0 \ll kT$ :

In this case we can apply the Debye-Hückel approximation

$$V_R^\psi = \frac{2n^0kT}{\kappa} \left(\frac{ze\psi_0}{kT}\right)^2 \left[1 - \tanh\left(\frac{\kappa D}{2}\right)\right] \quad (6.52)$$

- Most convenient in applications are:

$$V_R^\psi = \frac{32n^0kT}{\kappa} z^2 \left[1 - \tanh\left(\frac{\kappa D}{2}\right)\right] \quad (6.53)$$

$$V_R^\sigma = \frac{2n^0kT}{\kappa} \left(2y_0 \ln \left[ \frac{B + y_0 \coth(\kappa D/2)}{1 + y_0} \right] \right) \quad (6.54)$$

$$- \ln \left[ y_0^2 + \cosh(\kappa D) + B \sinh(\kappa D) + \kappa D \right] \quad (6.55)$$

where  $y_0 = ze\psi_0/kT$  and  $B = \left[1 + y_0^2 \cosh^2(\kappa D/2)\right]^{1/2}$

- Illustrations:

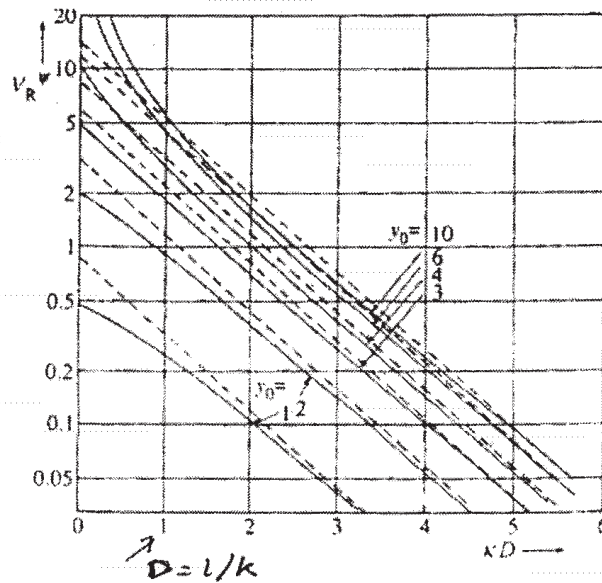
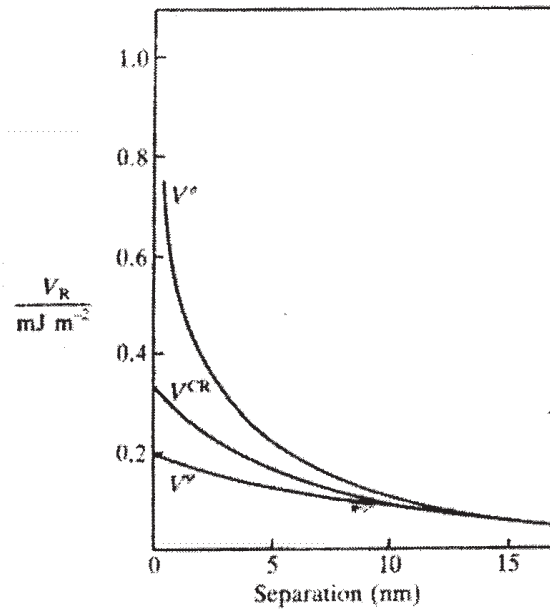
The figure above shows a comparison of the three repulsive potentials. The one for constant charge is clearly the largest, while the charge regulation solution is somehow intermediate. The next figure shows that  $V_R^\psi$  decreases with distance and with  $y_0 = ze\psi_0/kT$ . The approximate expression for  $D \gg 1/\kappa$  (dotted) is compared with exact solution (solid).

### Electrical Charge of a Surface

The most common way to bring charges on the surface of particles is to adsorb ionic surfactants. These can be salts which are fully dissociated (e.g. sodium dodecylsulfonate) or weak acids (e.g. carboxylic acids) that dissociate to an extent which depends upon the solution pH.



**CHAPTER 6. STABILITY OF COLLOIDAL SUSPENSIONS**



Another possibility is to act on the concentration of the so-called potential determining ions, as we discuss next.

When considering a dispersion of solid AgI particles in water, since the solution is saturated

**CHAPTER 6. STABILITY OF COLLOIDAL SUSPENSIONS**

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we have:

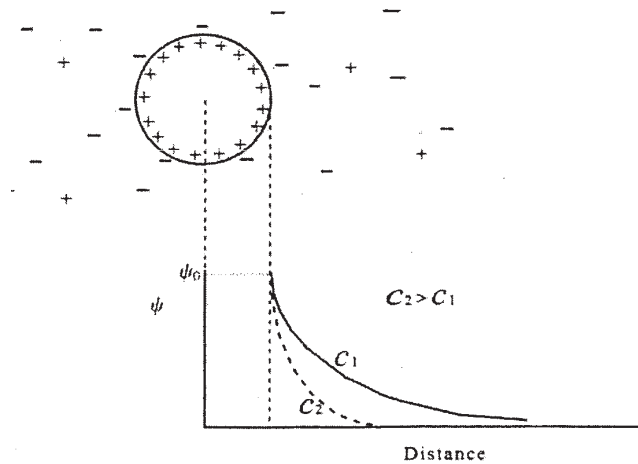
$$a_{\text{Ag}^+}^e a_{\text{I}^-}^e = K_S \tag{6.56}$$

where  $K_S$  is the solubility product. In addition, due to the solid-liquid equilibrium we have that the activities of each ion are equal in the two phases:

$$a_{\text{Ag}^+}^e = a_{\text{Ag}^+}^s \tag{6.57}$$

$$a_{\text{I}^-}^e = a_{\text{I}^-}^s \tag{6.58}$$

This in general implies that, since the affinity of  $\text{Ag}^+$  and  $\text{I}^-$  to the solid and solution is different, the particle acquires a charge. We can affect such particle charge by acting on the activity of the ions in the solution. If we add  $\text{AgNO}_3$ , then  $a_{\text{Ag}^+}$  in solution increases and  $a_{\text{I}^-}$  has to decrease, thus increasing the positive particle charge. In this case  $\text{Ag}^+$  and  $\text{I}^-$  are the potential-determining ions, and we can use them to control the particle charge and potential. The figure below shows the potential profile and the counterion distribution around a charged particle: they have to follow the potential distribution but thermal diffusion tends to uniformize them, the result is the diffusive electrical double layer. The thickness of this layer can be decreased by adding some other electrolyte, i.e., indifferent ions, as shown in the figure. This is the double layer compression which decreases the particle stability.



### 6.2.3 Total Interaction Energy

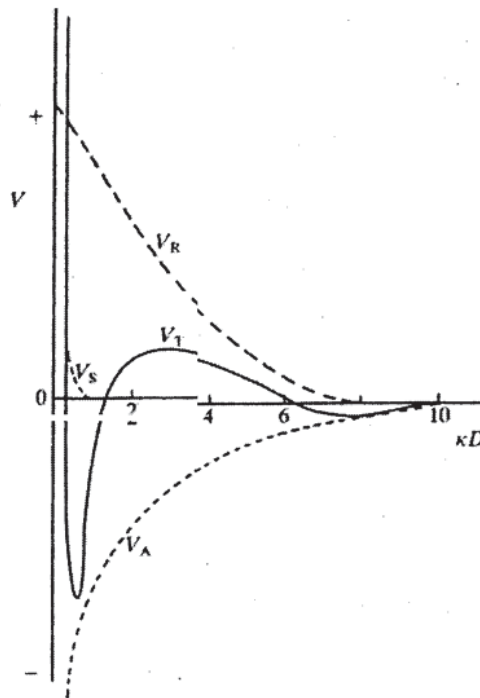
The total potential energy of interaction is given by the sum of the attractive and the repulsive contributions derived earlier:

$$V_T = V_A + V_R \quad (6.59)$$

Using expressions developed for flat surfaces and symmetric electrolyte, we get:

$$V_T = -\frac{A}{12\pi D^2} + \frac{32n^0kT}{\kappa} z^2 \left[ 1 - \tanh\left(\frac{\kappa D}{2}\right) \right] \quad (6.60)$$

which is illustrated in the figure on the next page. It is seen that the van der Waals forces dominate at low distances, where however  $V_T$  does not go to  $-\infty$ , but contrary increases due to the occurrence of Born repulsion forces, which are very short-range and come into play when the atom of the two surfaces come in contact. This leads to the very deep attractive well, referred to as primary minimum. At high distances, the van der Waals forces prevail again, often leading to the formation of a secondary minimum.

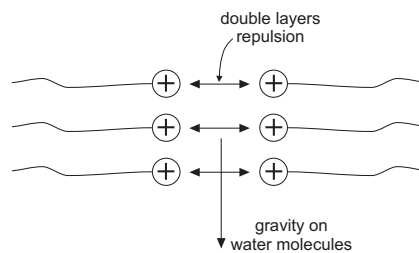


**Note**

Because of the large depth of the primary minimum the energy barrier for separating two particles is much larger, often substantially infinite, compared to that corresponding to the reverse process.

**6.2.4 Simple Manifestation of Electrical Double Layers: Soap Films**

The figure shows a soap film, where the water molecules are kept in the film by the repulsive forces between the layers of surfactant molecules adsorbed at the air-liquid interface.



For the film formed with a wire frame in the figure, at each height,  $H$  the hydrostatic pressure ( $H\rho g$ ) which tends to drain the water molecules have to be balanced by the double-layer pressure, which corresponds to a certain thickness of the film,  $D$  that can be measured. For example at height of about  $H = 10$  cm, the repulsive double-layer pressure has to be of the order of  $10^3$  N/m<sup>2</sup>. Soap film thickness of about 20 nm were stabilized by the overlapping diffusive double layers with  $\psi_0 \approx 30$  mV.

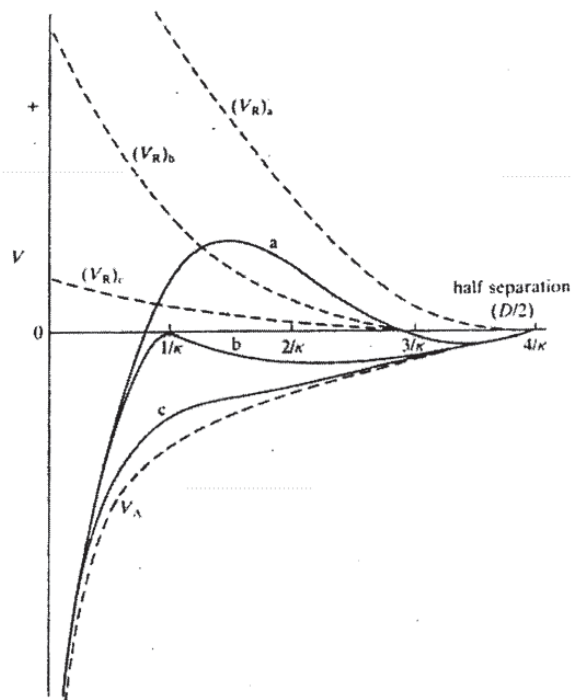
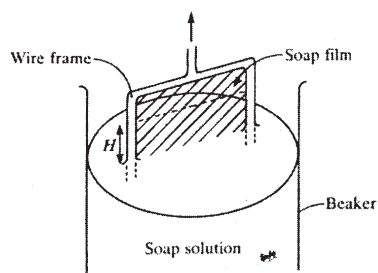
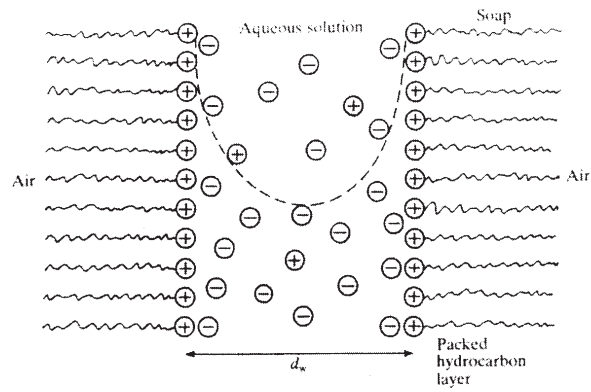
**6.3 Coagulation of Colloidal Suspensions**

From the shape of the total interaction potential curve as a function of particle distance we can define the stability of a colloid or a latex. This is illustrated in the figure below, where we have:

- a = kinetically stable or meta-stable colloid;
- b = marginally unstable (critical condition)
- c = unstable

The loss of stability, or particle aggregation, can be induced in two ways as described in the following.

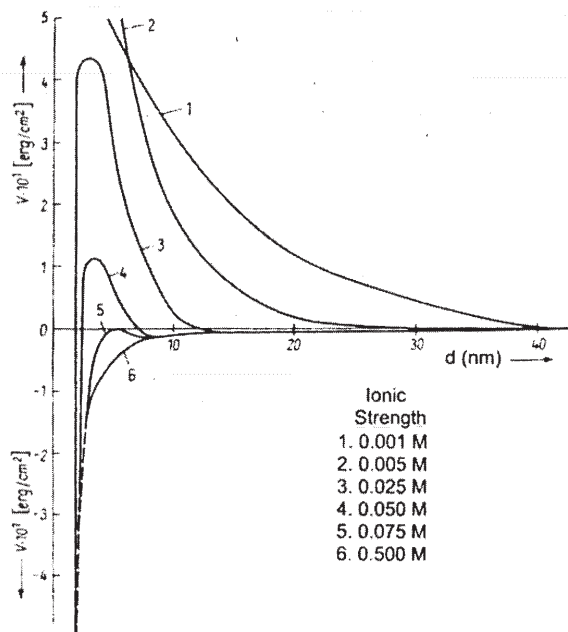
**CHAPTER 6. STABILITY OF COLLOIDAL SUSPENSIONS**



### 6.3.1 Aggregation by Potential Control

We can change the particle charge, and then its potential, as shown by the curves in the previous figure. This can be done by changing the activity of the potential determining ions. An example is given by the titration of a solution containing  $I^-$  using  $AgNO_3$ , based on the very low solubility of  $AgI$ . The first particles of  $AgI$  precipitated are in equilibrium with an excess of  $I^-$  in solution, therefore have a strong negative charge and are small and stable. This leads in fact to a milky dispersion. As we add more  $AgNO_3$ , more  $AgI$  precipitates and therefore the excess of  $I^-$  in solution decreases, together with the particle negative charge and stability. The colloidal particles start to aggregate leading to large flocs of  $AgI$ , which become visible. At some point the charge of the particle becomes zero, and after that they acquire a positive charge. By measuring particle migration in an electric field the potential at zero particle charge is found to be at  $Ag^+ = 3.2 \times 10^{-6}$  M, which being  $K_S = 8 \times 10^{-17}$ , corresponds to  $I^- = 2.5 \times 10^{-11}$  M which is very small as required for titration.

### 6.3.2 Aggregation by Electrolyte Addition



Even if the concentrations of the potential determining ions are such as to give a good sur-

**CHAPTER 6. STABILITY OF COLLOIDAL SUSPENSIONS**

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face charge, and therefore stability to the particles, we can induce aggregation acting on the indifferent ions, that is causing the double layer compression. This is shown in the figure above, where we see that as the concentration of the indifferent electrolyte increases, the energy barrier decreases and eventually becomes zero. At this point there is no opposition to aggregation, which becomes very fast and controlled by Brownian diffusion. The smallest electrolyte concentration leading to such a fast coagulation is called critical coagulation concentration. Typical values for three different colloids are reported in the table below:

Valency of counterions	Sol of As <sub>2</sub> S <sub>3</sub> negatively charged		Sol of Au negatively charged		Sol of Fe(OH) <sub>3</sub> positively charged	
Monovalent	LiCl	58			NaCl	9.25
	NaCl	51	NaCl	24	1/2BaCl <sub>2</sub>	9.65
	KNO <sub>3</sub>	50	KNO <sub>3</sub>	23	KNO <sub>3</sub>	12
Divalent	MgCl <sub>2</sub>	0.72	CaCl <sub>2</sub>	0.41	K <sub>2</sub> SO <sub>4</sub>	0.205
	MgSO <sub>4</sub>	0.81	BaCl <sub>2</sub>	0.35	MgSO <sub>4</sub>	0.22
	ZnCl <sub>2</sub>	0.69			K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	0.195
Trivalent	AlCl <sub>3</sub>	0.093				
	1/2Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.096	1/2Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.009		
	Ce(NO <sub>3</sub> ) <sub>3</sub>	0.080	Ce(NO <sub>3</sub> ) <sub>3</sub>	0.003		

It is seen that the ccc values seem to be independent of the electrolyte type but strongly affected by the charge of the counterion. The value of the ccc can be computed from a suitable expression of  $V_T(D)$  by imposing the two conditions for criticality:

$$V_T = 0 \quad \text{and} \quad \frac{dV_T}{dD} = 0 \tag{6.61}$$

Let us consider the case of flat surfaces with small overlapping ( $\kappa D > 1$ ):

$$V_T = -\frac{A}{12\pi D^2} + \frac{64n^0 kTZ^2}{\kappa} \exp(-\kappa D) \tag{6.62}$$

By setting

$$V'_T = \frac{2A}{12\pi D^3} - \kappa \frac{64n^0 kTZ^2}{\kappa} \exp(-\kappa D) = 0 \tag{6.63}$$

and substituting in the equation  $V_T = 0$ , we get

$$\frac{2A}{12\pi D^3} - \kappa \frac{A}{12\pi D^2} = 0 \Rightarrow \frac{2}{D} - \kappa = 0 \Rightarrow \kappa D = 2 \tag{6.64}$$

Substituting in the relation  $V_T = 0$ , we get the critical  $\kappa$ :

$$\kappa^3 = \frac{(4 \cdot 12 \cdot 64)\pi n^0 kT Z^2 \exp(-2)}{A} \quad (6.65)$$

and recalling for symmetrical electrolytes  $z = z_+ = z_-$

$$\kappa^2 = \frac{\sum n_i^0 z_i^2 e^2}{\epsilon_w kT} = \frac{2N_A z^2 e^2}{\epsilon_w kT} C_s \quad (6.66)$$

where  $C_s = n_i^0/N_A$  is the molar electrolyte concentration, it follows

$$\text{ccc}[\text{mol/L}] = \frac{(384)^2 (4\pi)^2 \epsilon_w^3 (kT)^5 Z^4}{2 \exp(4) N_A A^2 (ze)^6} \quad (6.67)$$

which at 25°C in water for relatively high potential so that  $Z \approx 1$ , reduces to

$$\text{ccc} = \frac{87 \cdot 10^{-40}}{z^6 A^2} \quad [\text{mol/L}] \quad (6.68)$$

This relation, although approximated, correctly predicts that the ccc value depends only on the charge of the electrolyte and in a rather strong way. This is known as the Schultz-Hardy rule. Its reliability is clearly demonstrated by the data shown in the table, where for the colloid  $\text{As}_2\text{S}_3$  we have that the ccc values for mono, di and trivalent electrolytes can be scaled as follows:

$$50 : 0.7 : 0.09 \approx 1 : 0.014 : 0.0018 \quad (6.69)$$

which compare well with the equation prediction  $1 : 2^{-6} : 3^{-6} = 1 : 0.016 : 0.0014$ . It is confirmed that the type of electrolyte, if the valency is the same, plays a minor role.

**Note**

Since the stability behavior of colloids is dominated by the concentration of the counterion, we can restrict our attention to symmetric electrolytes. Then,  $\text{MgCl}_2$  would behave like a 2:2 electrolyte in the presence of negatively charged surfaces, and like a 1:1 electrolyte in the presence of positively charged surfaces. This is confirmed by the ccc data reported in the previous table.

## 6.4 Steric Interactions

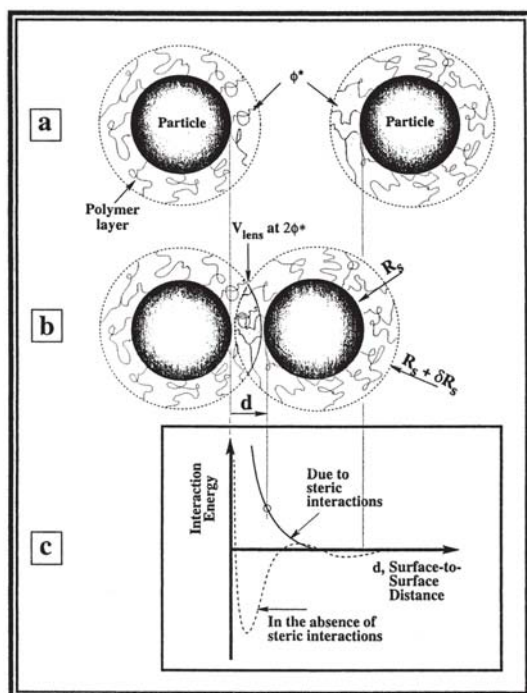
Steric interactions are the third important type of interactions between colloidal particles. Steric interactions are commonly used to stabilize particles when long term stability is required. The most common way to achieve steric stabilization is to graft some polymer on



## CHAPTER 6. STABILITY OF COLLOIDAL SUSPENSIONS

the particle surface. The grafting can be achieved in various ways. The most common is to add polymer to a solution of particles and let it attach onto the particle surface. However, the amount of polymer to be added has to be accurately chosen, otherwise unwanted destabilization effects (instead of stabilization) such as depletion induced flocculation or bridging flocculation can arise. Recently, another method has been developed, which consists in growing a polymer brush directly from the particle surface.

The physical mechanism underlying steric stabilization is strongly related to the thermodynamic behavior of polymers in solutions. The simplest theory used to explain this mechanism is the Flory-Krigbaum theory. As two particles coated with a polymer layer approach each other, when the center-to-center distance is small enough there is an overlap between the polymer layers. This overlap generates a change in the free energy of the polymer layers. There are two contribution of the free energy of the solution: the first one is a mixing contribution, the second one is an elastic contribution to the free energy. For the first case, if the polymer volume fraction in an isolated layer is equal to  $\phi$ , then the overlapping leads to a concentration of  $2\phi$  in the lens region, as depicted in the figure.



Polymer chains, if soluble in a solvent, occupy a large amount of volume, and their conformation is that of a random coil. If the degree of polymerization of the coil is equal to  $n$ , the

size of the coil scales as  $R \sim n^{0.5}$ . Therefore, if a chain is trying to occupy the same volume already occupied by another chain, there is usually an increase in the free energy of the system. The change in free energy resulting from the overlap of two sterically stabilized particles is equal to:

$$\Delta G = \Delta G_{\text{ov}} V_{\text{lens}} \quad (6.70)$$

The first term on the right hand side is the free energy change per unit volume, while the second term is the volume of the lens where the overlap occurs. The volume of the lens is a pure geometrical term, and is equal to:

$$V_{\text{lens}} = \frac{2\pi}{3} \left( \delta R_s - \frac{d}{2} \right)^2 \left( 3R_s + 2 * \delta R_s + \frac{d}{2} \right) \quad (6.71)$$

where  $d$  is the surface to surface distance between the cores of the particles,  $\delta R_s$  is the outer radius of the shell and  $R_s$  is the radius of the core (see the previous Figure). The free energy of overlap per unit volume is equal to:

$$\Delta H_{\text{ov}} = 2kT \left( \frac{\bar{V}_2^2}{\bar{V}_1 V_d^2} \right) \left( \frac{1}{2} - \chi \right) \quad (6.72)$$

where  $V_d$  is the volume occupied by a polymer coil,  $\bar{V}_1$  is the solvent molar volume, and  $\bar{V}_2$  is the polymer molar volume. It is important to note that the sign of the free energy of mixing per unit volume depends on the parameter  $\chi$ . In units of  $kT$ , the parameter  $\chi$  is a measure of the energy change between solvent-monomer interactions and solvent-solvent and monomer-monomer interactions. Mathematically this is expressed as follows:

$$\chi = \frac{z}{2kT} (2w_{12} - w_{11} - w_{22}) \quad (6.73)$$

where  $z$  is the coordination number of a monomer (or solvent) molecule, and  $w_{ij}$  is the energy of interaction between molecule  $i$  and molecule  $j$ . Here 1 are solvent molecules and 2 are monomer molecules. Therefore, depending on whether the monomer units like more solvent molecules rather than other monomer units, the  $\chi$  parameter can become smaller or larger than  $1/2$ . When  $\chi > 1/2$  we are in the presence of a bad solvent, i.e., the monomer units prefer to stay close to each other because the polymer is not soluble under those conditions in that solvent. This means that the free energy given by equation (6.72) is negative. In this case, interpenetration of polymer shells is favored, and the polymer does not provide a good stabilization. If instead  $\chi < 1/2$  the free energy given by equation (6.72) is positive,

and interpenetration is unfavorable. In that case, steric stabilization is effective. It is quite common that the quality of solvent can be changed for many polymers by simply playing with the temperature. In fact, the following temperature dependence of the  $\chi$  parameter on the temperature is usually observed:

$$\frac{1}{2} - \chi = \psi \left( 1 - \frac{\Theta}{T} \right) \quad (6.74)$$

where  $\Theta$  is the famous Theta temperature.  $T > \Theta$  implies a good solvent, while  $T < \Theta$  implies a poor solvent.  $T = \Theta$  is the critical solubility temperature for many solvents.

The second contribution to steric stabilization, arising when two polymer shells try to interpenetrate, is the elastic contribution. This mechanism underlying elastic stabilization is actually an entropic one, since polymer coils tend to assume in absence of any constraint a rather swollen configuration. By compressing a polymer, one limits their degrees of freedom and this reduction in configurational entropy generates a force that for small compressions can be approximated as obeying Hook's law, with an elastic constant equal to:

$$\Delta S_{ov} \propto k_H d, \text{ where } k_H = \frac{3kT}{nl^2} \quad (6.75)$$

where  $n$  is the degree of polymerization of a chain and  $l$  is approximately the length of a monomer unit. The contribution to the total free energy given by this mechanism is always positive, which means that compression of a polymer coil is always an unfavorable process.

When both contributions to steric stabilization are considered together, it turns out that in the case of a good solvent, steric interactions are always strongly repulsive. In the case of bad solvents, instead, attractive interactions dominate initially, but when the distance between the particle surface is further reduced, repulsion due to elastic compression eventually prevails.