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Interaction between colloidal particles

Literature Review

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Abstract

This report summarises the commonly accepted theoretical basis describing interaction between colloidal particles in an electrolyte solution. The two main forces involved are the van der Waals attractive force and the electrical repulsive force. The report describes in some depth the origin of these two forces, how they are formulated mathematically as well as how they interact to sometimes result in attraction and sometimes in repulsion between particles. The report also addresses how the mathematical models can be used to quantify the forces and under which conditions the models can be expected to give fair description of the colloidal system and when the models are not useful. This report does not address more recent theories that still are discussed as to their applicability, such as ion-ion correlation effects and the Coulombic attraction theory (CAT). These and other models will be discussed in future reports.

Sammanfattning

Denna rapport sammanfattar de vanligaste etablerade teorierna och modellerna som beskriver samverkan mellan kolloidala partiklar i elektrolytlösningar. De två viktigaste krafterna är den attraktiva van der Waals-kraften och kraften orsakad av elektrostatiska effekter. Rapporten går igenom och beskriver detaljerat hur dessa krafter uppstår, hur de kan formuleras i matematiska modeller liksom hur de samverkar för att ibland attrahera och ibland repellera partiklar. Rapporten beskriver hur de matematiska modellerna kan användas för att kvantifiera krafterna och under vilka omständigheter modellerna kan förväntas ge en rimlig beskrivning av kolloidala system och när modellerna inte är användbara. Denna rapport behandlar inte nyare teorier vilkas tillämpbarhet fortfarande diskuteras såsom jon-jon korrelationseffeter och Coulombisk attraktions teori (CAT). Dessa och andra modeller kommer att behandlas i kommande rapporter.

Contents

1 Introduction

In this report, we are concerned with particle-particle interactions, and the focus is put on the main forces that may operate between colloidal particles dispersed in a liquid.

By the term, "pair-interaction", we mean interaction between two particles, embedded in an infinitely large amount of electrolyte solution acting as the environment. Basically, we consider the components of the Gibbs and/or Helmholtz energy and the disjoining pressure, respectively, quantifying them as far as possible for plate-like particles for a range of conditions.

For two parallel plates, at a distance s apart, the disjoining pressure $\Pi(s)$ is the amount by which the normal component of the pressure tensor exceeds the outer pressure. If both plates are infinitely large, it would be the force between unit area of the one plate and the other infinite large plate. Thermodynamically, depending on the process conditions, the Gibbs energy $G_\mathrm{a}(s)$ or the Helmholtz energy $F_\mathrm{a}(s)$ is the isothermal reversible work of bring these two surfaces from an infinite distance to distance s apart. From that we find, for parallel flat plates,

$$\Pi(s) = -\left.\frac{\partial G_\mathrm{a}(s)}{\partial s}\right|_{p,T} \tag{1-1}$$

or

$$\Pi(s) = -\left.\frac{\partial F_\mathrm{a}(s)}{\partial s}\right|_{V,T} \tag{1-2}$$

For isolated pair interactions in incompressible systems, these two functions are identical. Therefore, we shall generally consider the Gibbs energy G_a due to the process conditions chosen. However, if we want to consider pair interactions in confined geometries or the interaction between a pair selected from a large collection of particles, the Helmholtz energy is the appropriate choice. Then G_a and F_a may differ significantly.

With this knowledge at hand, we shall now briefly review and discuss some types of interactions in some depth.

London-Van der Waals or dispersion interaction

These forces are ubiquitous; they depend on the nature of the particles and the medium, and on the geometry of the particles. As a first approximation, we can write the Van der Waals contribution to the Gibbs energy of interaction between two particles, a distance s apart, as,

$$G_{\mathrm{a,VdW}} = -A_{12\,(3)}\,f\,(\text{geometry}, s) \tag{1-3}$$

where $A_{12(3)}$ is the Hamaker constant for the interaction between particles of nature 1 and nature 2, respectively, across the medium 3.

For homo-interaction (material 1 identical to material 2), with Hamaker constants of the type $A_{11(3)}$, $G_{\mathrm{a,Vdw}} < 0$ (attractive). For hetero-interaction the Hamaker constant can, in a few situations, be negative. In practice, such situations occur most often when one of the components is a vapour.

Electrostatic interaction

The origin of these forces is double layer overlap. One of the most striking features of double layers is the very strong influence that indifferent electrolytes exert: they reduce ψ^d, the potential of the outer Helmholtz plane (i.e. the potential of the diffuse part of the double layer), and compress that layer (i.e. the Debye length κ^{-1} is reduced). As electro-static interaction is mainly determined by the diffuse parts of the double layers, this synergistic electrolyte effect makes itself strongly felt in the stability of hydrophobic colloids. This is the origin of the Schulze-Hardy rule.

The trend is that two isolated particles with the same charge sign repel each other. An exception to this rule takes place when one particle is highly charged, but the other only slightly. In this case, upon approach, even when both charges have the same sign, the higher charged one may induce a reverse charge onto the other, followed by attraction.

Unlike Van der Waals attraction, the electrostatic contribution to the Gibbs energy of interaction, $G_{a,el}$, is independent of the nature of particles, at a given charge or potential; on the other hand, $G_{a,VdW}$ is virtually insensitive to electrolytes and, for that matter, insensitive to the presence of a double layer.

Expressions for $G_{a,el}$ vary widely, depending on the geometry of the system, strong or weak overlap, high or low electrolyte concentration, etc, but for weak overlap and low potentials many of them have this shape:

$$\mathrm{G}_{a,\,el} = f\,(\mathrm{DL})(\psi^{d})^{2}\exp(-\kappa h) \qquad (1\text{-}4)$$

where f(DL) contains properties of the two double layers, and solution- and geometrical quantities (such as the dielectric permittivity and particle size), whereas h is the distance between the two outer Helmholtz planes, which is shorter than s in Equation 1-3 by an amount of twice the Stern layer thickness.

From $G_{a,el}$, the disjoining pressure Π_{el} can be obtained by differentiation with respect to h, but there are also ways to compute Π_{el} directly. Obviously, the exponential factor in Equation 1-4 stems from the exponential potential decay of the isolated diffuse double layer. On the other hand, equations such as the one above often contain ψ^{d} rather than the surface potential ψ^{0}; this is so, because it is the overlap of the diffuse parts which is most important. This has a historical background. In the original theory, as developed independently by Deryagin and Landau, and by Verwey and Overbeek, the conscious assumption was made that, upon interaction, the surface potentials on the particles would remain constant and equal to their values at infinite separation of the particles. As these authors ignored Stern layers, their surface potential ψ^{0} is often replaced by our ψ^{d}, which explains the appearance of this potential in the above equation. At the same time, the distances h and s were set equal. In reality, the process is much more complicated; upon interaction, the charge- and potential distribution over the Stern- and diffuse parts will change. This process is called regulation. In addition, diffuse double layer potentials are not directly measurable. However, experience has shown that the replacement of ψ^{d} by the electrokinetic potential ζ is often warranted, where the potentials ψ^{d} and ζ are those for isolated particles.

Generally speaking, electrostatic interaction is an important feature, and we shall have to pay much attention to it.

Steric interaction

These interactions are caused by macromolecules and can be repulsive or attractive. It is anticipated that the steric contribution to the Gibbs energy of interaction, $G_{a,ster}$, can be very high, tending to outweigh electrostatic repulsion, depending on its range of action. Particularly in systems with weak double layers (as for dispersions in nonaqueous media of low polarity) steric stabilization is often the sole mechanism that keeps particles apart, whereas depletion flocculation is relatively weak.

Since the particles we are mostly concerned with are clay particles, we shall not pay any attention on steric forces in this report. However, it should be stressed that steric, electric, and dispersion forces are not additive at all. Polymer trains modify the composition of the Stern layer, and hence the potential ψ^{d}. For random (homo)polymer adsorption the volume fraction in loops and tails is usually low enough for us to ignore its influence on the diffuse part of the double layer. Further, enrichment of polymer on surfaces modifies the Hamaker constant $A_{12(3)}$ and the effective s, because a third phase is introduced.

Magnetic interaction

This represents a special case, but when such forces are operative they often outweigh other interactions. It is very difficult to stabilize colloids against magnetic attraction. We shall not discuss magnetic colloids.

Solvent structure-mediated interaction

We will use this, admittedly somewhat clumsy, term to cover all interaction phenomena caused by the structure of the intervening liquid, insofar as it is modified by the presence of a surface. Structural modification near a hard wall includes the density oscillations, reorganization caused by hydrogen bonding to the solid, or by hydrophobic dehydration. In the literature these phenomena come under a hotchpotch of names, reflecting the specific interpretation the various authors have in mind, such as "water structure forces", "structural forces", "hydration forces", or even "acid-base interactions". Sometimes these names reflect the inability to interpret certain observed phenomena quantitatively in terms of well-understood interactions. In fact, solvent structure-mediated interactions are current subjects of study. Some aspects are reasonably well understood (e.g. the density oscillations have been reproduced in the surface force apparatus), others have alternative interpretations.

Approximately, however, an empirical formula can be given as,

$$G_{\mathrm{a,\,str}} = K_{\mathrm{str}}\,\lambda \exp(-s/\lambda) \qquad (1\text{-}5)$$

in which λ is of the range of molecular interactions in the solvent.

Are these forces additive? The answer is not unequivocal, since it depends on the kinds of forces involved and on the dynamics of interaction. For practical purposes, dispersion and electrostatic forces are additive. By the term, "practical purposes", we mean that, in practice, interaction forces can rarely be measured with an absolute accuracy of better than 5%, and that we therefore do not have to worry about non-additivities smaller than that. The most obvious deviation from additivity arises when there is steric interaction in combination with double layer overlap, because then the ionic charge distribution and its dynamics will be affected by the absorbed train and loop segments.

In this report, we shall discuss Van der Waals interactions between molecules in Chapter 2, and then Van der Waals interactions between macrobodies in Chapter 3. Following these, we shall focus on the models available for electric double layers in Chapter 4, and the theories for double layer overlap in Chapter 5. Solvent structure-mediated interactions will be briefly reviewed and discussed in Chapter 6, and the extended DLVO theory will be presented in Chapter 7.

2 Attraction between molecules

Nowadays, it is generally accepted that there are three types of attractive interactions between any pair of molecules, known as Keesom-Van der Waals, Debye-Van der Waals, and London-Van der Waals or dispersion forces. These forces are collectively called Van der Waals forces, and they are ubiquitous in nature /1/.

2.1 Attraction in a vacuum

As we shall discuss in more detail below, the Keesom- and Debye-Van der Waals forces are classical in the sense that they can be fully understood and interpreted in terms of classical electrostatics. Dispersion forces are, however, of a quantum mechanical nature and the London Equation, describing the attraction between two induced dipoles, could be derived only after the advent of quantum mechanics.

2.1.1 Keesom-Van der Waals forces

Keesom-Van der Waals forces are interactions between pairs of polar molecules. Inside each of the polar molecules a spontaneous separation of positive and negative charge has taken place. Thus, polar molecules have permanent dipoles as a property, and they can attract or repel each other electrostatically, depending on their spatial orientation. If two free polar molecules approach each other, attractive orientations are energetically more likely than repulsive ones, so that statistically they prevail.

To start with, let us now consider two dipoles that are in fixed position with respect to each other in a vacuum. The electric field strength $\mathbf{E}_1$ of the first dipole with a dipole moment of $\mathbf{p}_1$ can be written as /2/,

$$\mathbf{E}_1 = \frac{3(\mathbf{p}_1 \cdot \mathbf{r})\mathbf{r}}{4\pi\varepsilon_0 r^5} - \frac{\mathbf{p}_1}{4\pi\varepsilon_0 r^3} \qquad (2\text{-}1)$$

where $\mathbf{r}$ is counted with respect to the centre of the first dipole.

The electric energy of the second dipole with a dipole moment of $\mathbf{p}_2$ then reads /1, 2/,

$$\Phi_2 = -\mathbf{p}_2 \cdot \mathbf{E}_1 \qquad (2\text{-}2)$$

If the two dipoles reside on molecules 1 and 2, respectively, they would be free to rotate and statistical averaging of the interaction energy over all spatial orientations of the two dipoles would be required. This could be done by considering that in a thermal average the low energy configurations occur preferentially determined by a Boltzmann weighting factor. Thus, the interaction energy of molecule 2 can be given by /3/,

$$\Phi_{\mathrm{K2}} = \frac{1}{4\pi}\int \Phi_2 \exp\left(-\frac{\Phi_2}{k_{\mathrm{B}}T}\right)\mathrm{d}\Omega \qquad (2\text{-}3)$$

where the integration is performed over polar angle, θ, and azimuthal angle, ϕ, with,

$$\mathrm{d}\Omega = \sin\theta\mathrm{d}\theta\mathrm{d}\phi \qquad (2\text{-}4)$$

and when integrated over all orientations, $\mathrm{d}\Omega$ gives 4π.

In the case of relatively weak interactions, we can expand the exponential function in Equation 2-3 as a power series. If only the zeroth- and first-order terms are retained, we have,

$$\Phi_{\mathrm{K2}} = \frac{1}{4\pi}\int\left(\Phi_2 - \frac{\Phi_2^2}{k_{\mathrm{B}}T}\right)\mathrm{d}\Omega \qquad (2\text{-}5)$$

At r.h.s. of the equation, the integration of the simple term vanishes because positive and negative values of the energy are equally possible. The integration of the quadratic term remains, however. Thus, combination of Equations 2-1, 2-2 gives,

$$\Phi_{\mathrm{K2}} = -\frac{p_1^2 p_2^2}{3(4\pi\varepsilon_0)^2 k_{\mathrm{B}} T r^6} \tag{2-6}$$

The same equation could be derived for the interaction energy of molecule 1 on which the first dipole resides.

Thus, the total energy of attraction is,

$$\Phi_{\mathrm{K}} = -\frac{2 p_1^2 p_2^2}{3(4\pi\varepsilon_0)^2 k_{\mathrm{B}} T r^6} \tag{2-7}$$

This is the Keesom Equation, and it applies to the interaction of two polar molecules.

2.1.2 Debye-Van der Waals forces

Debye-Van der Waals forces particularly mean attractions between polar and non-polar molecules. A non-polar molecule has no permanent dipole of its own. However, if it approaches a polar molecule, the electric field of which would induce an uneven charge distribution in it. The induced dipole is to be oriented in such a way as to attract the polar molecule. Since induction also takes place in polar molecules, Debye forces have to be added to the Keesom forces.

Let us now consider a dipole and a non-polar molecule that are in fixed position with respect to each other in a vacuum. The electric field produced by the dipole can also be quantitatively described by Equation 2-1 if we label it as “1”. The induced dipole moment, $\mathbf{p}_2$, is then proportional to the field $\mathbf{E}_1$ with the polarizability α_2 of the non-polar molecule, i.e.

$$\mathbf{p}_2 = \alpha_2 \mathbf{E}_1 \tag{2-8}$$

Intuitively one would expect that the polarizability will increase with molecular size, since in smaller molecules the electrons can be displaced over shorter distance and will be more tightly bound to the nuclei. In fact, the polarizability, reflecting to what extent the charges inside a molecule can shift, is proportional to the molecular volume.

With Equation 2-8 at hand, one may use Equation 2-2 to compute the electric energy of the induced dipole without any consideration. This is, however, wrong, because Equation 2-2 does not account for those part of energy that is necessary to polarize the neutral molecule. To tackle this problem appropriately, we should start from the definition of the dipole moment. Let there be in the polarized molecule charges $+q$ and $-q$ a distance d$\mathbf{r}$ apart, the dipole moment is then given by,

$$\mathbf{p}_2 = q\mathrm{d}\mathbf{r} \tag{2-9}$$

and the force acting on the induced dipole is,

$$\mathbf{F}_2 = q\mathrm{d}\mathbf{E}_1 \tag{2-10}$$

Thus, the electric energy of the induced dipole reads

$$\Phi_2 = -\int_{\infty}^{\mathbf{r}} \mathbf{F}_2 \cdot \mathrm{d}\mathbf{r} \tag{2-11}$$

Substitution of Equations 2-9 and 2-10 into it immediately yields,

$$\Phi_2 = -\int_{\infty}^{\mathbf{E}_1} \mathbf{p}_2 \cdot \mathrm{d}\mathbf{E}_1 \tag{2-12}$$

Then combination of Equation 2-8 and 2-12 gives,

$$\Phi_2 = -\int_{\infty}^{\mathbf{E}_1} \alpha_2 \mathbf{E}_1 \cdot \mathrm{d}\mathbf{E}_1 \tag{2-13}$$

The result is,

$$\Phi_2 = -\frac{1}{2}\alpha_2 E_1^2 \tag{2-14}$$

and it can be explicitly written as, following from Equation 2-1,

$$\Phi_2 = -\frac{\alpha_2 p_1^2}{2(4\pi\varepsilon_0)^2 r^6}\left(1 + 3\cos^2\theta\right) \tag{2-15}$$

If the dipole 1 resides on molecule 1, it would be free to rotate and statistical averaging of the interaction energy over all spatial orientations would be required. In this case, however, the polarizing and polarized molecules are always optimally aligned, because the electronic frequencies in an atom are orders of magnitude higher than those for the rotation of dipoles. Thus, spatially averaging goes to, for the interaction energy of the molecule 2,

$$\Phi_{\mathrm{D2}} = \frac{1}{4\pi}\int \Phi_2 \,\mathrm{d}\Omega \tag{2-16}$$

Substituting Equation 2-15 into it then yields,

$$\Phi_{\mathrm{D2}} = -\frac{\alpha_2 p_1^2}{(4\pi\varepsilon_0)^2 r^6} \tag{2-17}$$

Thus, as expected in view of the physical principles on which it rests, this expression contains the permanent dipole moment and the polarizability of the non-polar molecule, but not the temperature.

On the other hand, Debye forces also operate if the non-polar molecule is replaced by a polar one. Then, the second molecule induces a dipole in the first. The contribution to the interaction energy is identical to Equation 2-17 except that the subscripts are inter-changed. Taking the two as additive, the total energy of attraction is,

$$\Phi_{\mathrm{D}} = -\frac{\alpha_2 p_1^2 + \alpha_1 p_2^2}{(4\pi\varepsilon_0)^2 r^6} \tag{2-18}$$

This is the Debye Equation, which describes the attraction between a permanent and an induced dipole.

As we discussed earlier, Debye forces have to be added to those due to dipole-dipole interactions. The extent to which the two are additive depends, however, on the strength of the coupling between spontaneous and induced polarization /1/.

2.1.3 London-Van der Waals forces

London-Van der Waals or dispersion forces operate between non-polar molecules, and are of a quantum mechanical nature. Some impression can be obtained by considering molecules as having positive nuclei around which electrons circulate with an extremely high frequency. At every instant, the molecule is therefore polar, but the direction of this polarity changes with this high frequency. When two such "oscillators" now approach, they start to influence each other, as in the Keesom case, attractive situations having higher probabilities than repulsive ones. Because of the electrodynamic nature of this type of interaction, the information from the first oscillator to the second regarding its spatial orientation is transported with the speed of electromagnetic waves. This speed is very high but nevertheless it is finite and, if the atoms are far apart, there is a substantial delay in the response of the second oscillator to the orientation of the first one. Its phase lags behind that of the first atom. The result is that the attraction is relative weaker than it is at short distances and mathematically this results in a relatively more rapid decrease with distance.

Although this reasoning gives some feeling about the origin and nature of dispersion forces, fully understanding the interaction energy could be reached only after the advent of quantum mechanics. Therefore, we shall dispense with a rigorous examination of the situation involved and consider only the harmonic oscillator model and the final results.

As shown in Figure 2-1, the harmonic oscillator model works on a linear arrangement of two dipoles, whose length l_i is negligible compared to the distance between their centres, and whose moment p_i is equal to el_i in magnitude.

The dipoles are formed by symmetrical vibration of electrons in two dimensions in the two identical molecules, in which it is assumed that only the outer electron contributes to the polarizability. Then, combination of Equations 2-1 and 2-2 gives the interaction energy of two dipoles in this arrangement as /4/,

$$\Phi_1 = \pm \frac{2(el_1)(el_2)}{4\pi\varepsilon_0 r^3} \tag{2-19}$$

where positive sign applies for parallel dipoles, and negative sign for antiparallel dipoles.

In addition, each of the vibrating dipoles may be regarded as a harmonic oscillator, for which the potential energy is given by,

$$\Phi_2^{\mathrm{i}} = \frac{(el_{\mathrm{i}})^2}{2\alpha} \tag{2-20}$$

Combining these energy contributions we have the following expression to be used as the potential energy of this system,

$$\Phi = \frac{(el_1)^2}{2\alpha} + \frac{(el_2)^2}{2\alpha} \pm \frac{2(el_1)(el_2)}{4\pi\varepsilon_0 r^3} \tag{2-21}$$

When this energy function is substituted into the one-dimensional Schrödinger Equation and suitable mathematical operations are carried out, the allowed energy is found to be,

$$\psi = (n_1 + 1/2)h\xi_1 + (n_2 + 1/2)h\xi_2 \tag{2-22}$$

where $n = 0, 1, 2, \ldots$ is the vibrational quantum number, h is the Plank's constant and the macroscopic vibration frequencies are given by,

$$\xi_1 = v\left(1 - \frac{2\alpha}{4\pi\varepsilon_0 r^3}\right)^{1/2} \quad \text{and} \quad \xi_2 = v\left(1 + \frac{2\alpha}{4\pi\varepsilon_0 r^3}\right)^{1/2} \tag{2-23}$$

We observe that both ξ_1 and ξ_2 approach v as $r \to \infty$. Thus v is identified as the frequency of vibration for the system in the case where the electrons vibrate independently.

From Equation 2-22, we know that the lowest energy, ψ_1, for the two coupled oscillators is the situation in which $n_1 = n_2 = 0$, i.e.

$$\psi_1 = \frac{1}{2}h\left(\xi_1 + \xi_2\right) \tag{2-24}$$

and the energy of the two independent oscillators in their ground state is,

$$\psi_0 = 2 \times \frac{1}{2}hv \tag{2-25}$$

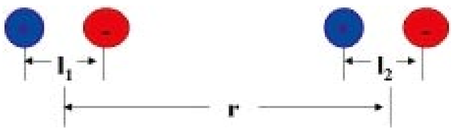

Figure 2-1. *A linear arrangement of two dipoles, used to define the potential energy in the Schrödinger equation for the London interaction energy.*

The difference between ψ_1 and ψ_0 gives then the contribution of dispersion forces to the interaction energy,

$$\Phi_\mathrm{L} = \frac{1}{2}h\left(\xi_1 + \xi_2 - 2\nu\right) \tag{2-26}$$

Substituting the expressions for ζ_1 and ζ_2, given by Equation 2-23, into this equation, we obtain the following result,

$$\Phi_\mathrm{L} = \frac{1}{2}h\nu\left[\left(1 - \frac{2\alpha}{4\pi\varepsilon_0 r^3}\right)^{1/2} + \left(1 + \frac{2\alpha_2}{4\pi\varepsilon_0 r^3}\right)^{1/2} - 2\right] \tag{2-27}$$

Expanding the square roots by the binomial expression and retaining no terms higher than second order yields,

$$\Phi_\mathrm{L} = -\frac{h\nu\alpha^2}{2(4\pi\varepsilon_0)^2 r^6} \tag{2-28}$$

When the molecules are capable of vibration in all three dimensions, the constant in the above expression becomes 3/4 rather than 1/2, i.e.

$$\Phi_\mathrm{L} = -\frac{3h\nu\alpha^2}{4(4\pi\varepsilon_0)^2 r^6} \tag{2-29}$$

When the molecules are unlike, their individual frequencies and polarizabilities should be involved, and the counterpart of Equation 2-29 is /1, 4/,

$$\Phi_\mathrm{L} = -\frac{3h}{2}\frac{\nu_1\nu_2}{\nu_1 + \nu_2}\frac{\alpha_1\alpha_2}{(4\pi\varepsilon_0)^2 r^6} \tag{2-30}$$

This is the London Equation, which describes the attraction between two induced dipoles that are not far apart.

2.1.4 Properties of Van der Waals forces

In examining the Keesom, Debye and London Equations we see that (1) they share as a common feature an inverse sixth-power dependence on the separation distance r, i.e. the interaction energy all decreases as r^{-6}, and (2) the molecular parameters describing the polarization of a molecule, polarizability and dipole moment, serve as proportionality factors in these expressions.

Due to the very different origin of dispersion interactions, however, London forces differ from the other two in two more respects. First, London interactions are to some extent additive, meaning that in large collections of molecules the total energy is not very different from the sum of the pair interaction energies. Secondly, London forces exhibit the phenomenon of retardation, meaning that, for large r, Φ_L decreases more rapidly with separation than at small r.

For very large separations ($r > c/\nu$) of two identical molecules, the total energy of the London interaction becomes /1/,

$$\Phi_\mathrm{R} = -\frac{23}{4\pi}\frac{hc\alpha^2}{(4\pi\varepsilon_0)^2 r^7} \tag{2-31}$$

where we use the subscript R instead of L to indicate that the London interaction is now retarded, and c is the speed of light in a vacuum.

For intermediate separations, there is gradual transition from the r^{-6} to the r^{-7} power law. Casimir and Polder /5/ wrote,

$$\Phi_\mathrm{R} = -\frac{3}{8\pi}\frac{h\omega\alpha^2}{(4\pi\varepsilon_0)^2 r^6} f\left(\frac{\omega r}{c}\right) \tag{2-32}$$

where $\omega = 2\pi\nu$ is the angular frequency, and the function at the r.h.s is a complicated integral but according to Overbeek /6/ it may be replaced by the following expressions:

$$f\left(\frac{\omega r}{c}\right)=\begin{cases}1.01-1.04\left(\dfrac{\omega r}{c}\right) & \text{for } 0<\dfrac{\omega r}{c}<3\\ 2.45\left(\dfrac{c}{\omega r}\right)-2.04\left(\dfrac{c}{\omega r}\right)^2 & \text{for } 3<\dfrac{\omega r}{c}\end{cases} \tag{2-33}$$

These are good approximations and useful for the calculation of retarded forces between macroscopic bodies. For short separation r, Equation 2-32 reduces to the London Equation 2-29 within 1%.

2.1.5 Superposition of Van der Waals forces

In general, we may think of any molecule as possessing a dipole moment and polarizability. This means that each of the three types of interaction may operate between any pair of molecules. Thus, we may write the total energy of Van der Waals attraction as,

$$\Phi_A = \Phi_K + \Phi_D + \Phi_L \tag{2-34}$$

For a pair of identical molecules, combination of Equations 2-7, 2-18, and 2-29 then gives,

$$\Phi_A = -\beta_{11} r^{-6} \tag{2-35}$$

with the interaction parameter given by,

$$\beta_{11} = \frac{1}{(4\pi\varepsilon_0)^2}\left(2\alpha p^2 + \frac{2}{3}\frac{p^4}{k_B T} + \frac{3}{4}h\nu\alpha^2\right) \tag{2-36}$$

where the subscript 11 has been added to β as a reminder that this result applies to a pair of identical molecules.

Of course, in non-polar molecules where $p = 0$, two of the three sources of attraction make no contribution to Φ_A. All molecules display, however, the dispersion component of attraction, because all are polarizable and that is the only requirement for the London interaction.

Not only is the dispersion component the most ubiquitous of the attractions, but it is also the most important in almost all cases. Only in the case of highly polar molecules such as water is the Keesom interaction greater than the dispersion component. Likewise, the mixed interaction described by the Debye Equation is generally the smallest of the three.

On the other hand, for interacting molecules in a vacuum or in a gas, retardation of the dispersion forces does not have to be accounted for, because retardation sets in only at distances where the forces are already so weak to become negligible. However, for the interaction between macrobodies, including colloids, retardation must often be taken into account.

2.2 Attraction in a medium

For two molecules 1 and 2, a certain distance apart in a medium 3, the Van der Waals forces between them are reduced as compared with the case in a vacuum or in a gas, because of the dielectric screening of the medium. For Keesom and Debye interactions, the force is reduced by a factor equal to the relative dielectric permittivity of the media ε_3 (as in Coulomb's law) due to their electrostatic origin. For London interactions, however, any screening of an intervening homogeneous medium cannot be accounted for in like manner, as elucidated clearly by McLachlan's work /7~10/.

2.2.1 The McLachlan formula

As a generalization, McLachlan extends the London Equation in two respects /7~10/. First, he takes into account that atoms and molecules may have more than one electron participating in the ionization, i.e. a number of frequencies ν may be needed for vibration of electrons around the nuclei. Secondly, he considers the consequences of a medium between the interacting molecules.

For non-retarded forces, he gives the following equation to describe the interaction energy in a medium,

$$\Phi_{\mathrm{M}} = -\frac{3h}{(4\pi\varepsilon_0)^2 \pi r^6} \int_0^\infty \frac{\alpha_1(i\nu)\alpha_2(i\nu)d\nu}{\varepsilon_3^2(i\nu)} \qquad (2\text{-}37)$$

It is noted that this expression has an r^6 in the denominator, as in the London Equation. However, the relative permittivity of the media ε_3 occurs squared and not linearly. In addition, the polarizabilities of the molecules, i.e. α_1 and α_2, are not constant anymore but depend on frequency ν, as does ε_3, and an integration over all frequencies has to be carried out in order to find the interaction energy Φ_{M}.

For retarded forces, he also gives an equation similar to Equation 2-37 but it contains an r^7 and an $\varepsilon_3{}^{5/3}$ in the denominator.

On the other hand, it could be shown that expression 2-37 would reduce to the London Equation 2-30 under the conditions for which the latter has been derived. Before we demonstrate this, however, it is better to understand more about dielectric permittivities and polarizabilities in an alternating electric field.

2.2.2 Dielectric permittivity

The frequency dependence of the relative permittivity, ε, could be well understood if we consider a polar molecule in an alternating electric field /1/.

Let the rotational relaxation time for dipole orientation be τ. If the frequency of the applied field (ν or ω) is low, that is if $\nu\tau << 1$, the dipoles can follow the alternations of the field; the medium is therefore continually polarized and as a result the permittivity is high. The system is then fully relaxed, and the value that the permittivity assumes under these conditions is called the static limit $\varepsilon(0)$ or the static relative permittivity or simply the dielectric constant.

Coulomb, Keesom and Debye forces require $\varepsilon_0\varepsilon(0)$ in the denominator if interaction in a homogeneous medium is considered.

When the frequency ν is increased to approach $1/\tau$, the dipole orientation starts to lag behind that dictated by the field. In mathematical language, **p** and **E** are no longer in phase. For such high frequencies that $\nu\tau >> 1$, the dipoles do not move anymore. Then the permittivity is constant again, but at a much lower value $\varepsilon(\infty)$ because the medium can now polarize only by electronic polarizations of the molecules. In the region around $\nu\tau \approx 1$, ε decreases with ν, as show in Figure 2-2 (curve ε'), and the frequency $\nu = 1/\tau$ is known as the resonance frequency. For permanent dipoles it is around 10^{11} Hz, and for electronic polarization around 10^{15} Hz, which is in the visible range of the spectrum.

Figure 2-2 contains another curve, $\varepsilon''(\nu)$, with a maximum equal to half of $\varepsilon'(0)+ \varepsilon'(\infty)$. This quantity is a measure of the conversion of the electrical energy of the applied field into heat, i.e. it measures the energy dissipation. Such dissipation is a maximum when the frequency of the field equals the resonance frequency of the dipoles; under those conditions, the dipoles can pick up most of the energy of the field and convert it into heat. For full alignment ($\nu\tau << 1$) or no alignment at all ($\nu\tau >> 1$), no energy is dissipated and $\varepsilon'' = 0$.

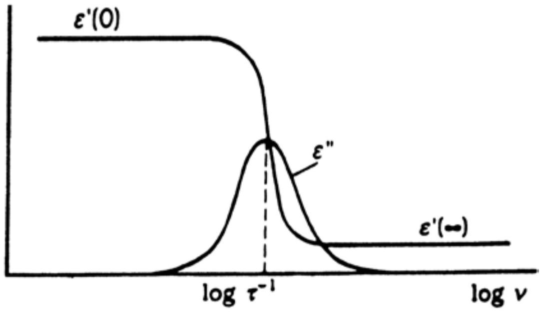

Figure 2-2. *Sketch of dielectric relaxation.*

It follows that under conditions where relaxation phenomena occur the quantity we have called "dielectric permittivity" virtually consists of two components, a contribution $\varepsilon'(v)$, which is a measure of the storage of applied energy by polarization (this part relaxes when the field is turned off) and a contribution $\varepsilon''(v)$, which is a measure of energy dissipation (which already relaxes when the field is on). Thus, in order to distinguish the storage and the dissipative part, we may write the total permittivity as,

$$\hat{\varepsilon}(v) = \varepsilon'(v) - \mathrm{i}\varepsilon''(v) \quad \text{or} \quad \hat{\varepsilon}(\omega) = \varepsilon'(\omega) - \mathrm{i}\varepsilon''(\omega) \tag{2-38}$$

The circumflex has been added as a reminder that this quantity is complex. The minus sign in this expression is not critical; it is a matter of mathematical convenience.

The complex permittivity is usually a complicated function of frequency, since it is a superimposed description of dispersion phenomena occurring at multiple frequencies. It could, however, be shown that $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ are actually related to each other in the following way,

$$\varepsilon'(\omega) = \varepsilon'(\infty) + \frac{\varepsilon'(0) - \varepsilon'(\infty)}{1 + \omega^2 \tau_\mathrm{r}^2} \tag{2-39}$$

and

$$\varepsilon''(\omega) = \frac{[\varepsilon'(0) - \varepsilon'(\infty)]\omega\tau_\mathrm{r}}{1 + \omega^2 \tau_\mathrm{r}^2} \tag{2-40}$$

where τ_r denotes the relaxation time of the system.

Thus, as a general phenomena and expressed by the famous Kramers-Kronig relations /11, 12/, we can write,

$$\varepsilon'(\omega) - \varepsilon'(\infty) = \frac{2}{\pi}\int_0^\infty \frac{x\varepsilon''(x)}{x^2 - \omega^2}dx \tag{2-41}$$

in which x is the dummy frequency variable over which ε'' has to be integrated in order to find $\varepsilon'(\omega)$. In vacuum $\varepsilon'(\infty) = 1$. The counterpart of Equation 2-41 is,

$$\varepsilon''(\omega) = -\frac{2\omega}{\pi}\int_0^\infty \frac{\varepsilon'(x) - \varepsilon'(\infty)}{x^2 - \omega^2}dx \tag{2-42}$$

Using the Kramers-Kronig relations, it is then possible obtain $\varepsilon''(\omega)$ from $\varepsilon'(\omega)$ and vice visa. Hence, after changing to imaginary frequencies, the integration in Equation 2-37 can be carried out.

2.2.3 Polarizability

According to its definition, the polarizability α is a measure of the extent to which electrons in an atom or molecule can adjust their orbitals in an applied field. If the field is static in the sense that the frequency is low as compared to the electronic vibrations and frequencies, the polarizability is a constant and approximately given by /1/,

$$\alpha \approx 4\pi\varepsilon_0 a^3 \tag{2-43}$$

in which a stands for the molecular radius.

Usually, we call this the polarizability. In the terminology of this section we could write it as $\alpha(0)$, the zero-frequency limit of $\alpha(\omega)$. In fact, most electronic vibrations are in the ultraviolet so that $\alpha(\omega)$ keeps its static value up to the visible range of the spectrum, as shown in Figure 2-3 for a typical molecule.

If the angular frequency of the external field is identical to the frequency ω_k of a given electron k, this electron could respond very well to the field, meaning that it can absorb energy from the field during every oscillation, so that its amplitude would rise without bounds, if no damping would take place. This phenomenon is an example of electronic resonance with resonance frequency $\omega = \omega_k$.

In general, a molecule may have many resonance frequencies. This implies that the polarizability is also frequency dependent and therefore we write $\alpha(\omega)$ instead of α. As, moreover, there is a storage part and a dissipative part, the latter determined by the damping, it becomes expedient to write α as a complex quantity, in the same way as for the dielectric permittivity as shown in Equation 2-38.

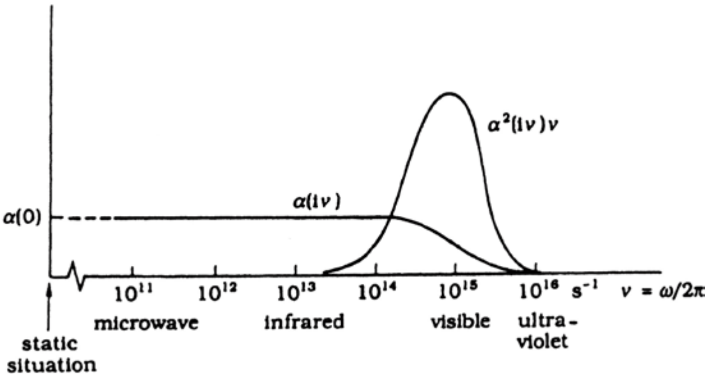

Figure 2-3. *Sketch of the frequency dependency of the polarizability and of the contributions of the various frequency ranges to the dispersion energy of interaction.*

Expressions for $\alpha(\omega)$ can be obtained by classical electron theory. For an assembly of k independent undamped oscillations Lorentz /1/ gives,

$$\alpha(\omega) = \frac{e^2}{m}\sum_{\mathrm{k}} \frac{f_{\mathrm{k}}}{\omega_{\mathrm{k}}^2 - \omega^2} \tag{2-44}$$

where f_{k} is the number of electrons oscillating with frequency ω_{k} and m the mass of the electron.

Equation 2-44 can also be derived quantum mechanically. Thus, below the visible light range, as $\omega << \omega_{\mathrm{k}}$, we may write,

$$\alpha(0) = \frac{e^2}{m}\sum_{\mathrm{k}} \frac{f_{\mathrm{k}}}{\omega_{\mathrm{k}}^2} \tag{2-45}$$

which, for only one oscillator with frequency ω_1, reduces to,

$$\alpha(0) = \frac{e^2}{m\omega_1^2} \tag{2-46}$$

Using classical mechanics, it can be shown that this expression is virtually equivalent to Equation 2-43, if we consider that the centrifugal force on the electron, circulating around the nuclei at a distance a, is balanced by the Coulomb attraction force. Hence, our expressions for the polarizability are consistent.

However, as damping is not accounted for, Equation 2-44 would predict infinitely high polarizabilities at the resonance frequency $\omega = \omega_{\mathrm{k}}$. To tackle this problem, an extension is required and this leads to,

$$\hat{\alpha}(\omega) = \frac{e^2}{m}\sum_{\mathrm{k}} \frac{f_{\mathrm{k}}}{\omega_{\mathrm{k}}^2 - \omega^2 + \mathrm{i}\omega\gamma_{\mathrm{k}}} \tag{2-47}$$

where γ_{k} is a constant, of dimensions s^{-1}, characterizing the extent of damping and it can be obtained experimentally from the width of the kth absorption band.

Now the polarizability is a complex quantity which, by analogy to Equation 2-38, can be written as,

$$\hat{\alpha}(\omega) = \alpha'(\omega) - \mathrm{i}\alpha''(\omega) \tag{2-48}$$

with

$$\alpha'(\omega) = \frac{e^2}{m}\sum_{\mathrm{k}} \frac{f_{\mathrm{k}}(\omega_{\mathrm{k}}^2 - \omega^2)}{(\omega_{\mathrm{k}}^2 - \omega^2)^2 + \omega^2\gamma_{\mathrm{k}}^2} \tag{2-49}$$

and

$$\alpha''(\omega) = \frac{e^2}{m}\sum_{\mathrm{k}} \frac{f_{\mathrm{k}}\,\omega\gamma_{\mathrm{k}}}{(\omega_{\mathrm{k}}^2 - \omega^2)^2 + \omega^2\gamma_{\mathrm{k}}^2} \tag{2-50}$$

We see that the real and imaginary part of $\alpha(\omega)$ are in principle accessible quantities. They are interrelated again by the Kramers-Kronig relations: Equations 2-41 and 2-42 also apply if $\varepsilon'(\omega) - \varepsilon'(\infty)$ is replaced by $\alpha'(\omega)$ and $\varepsilon''(\omega)$ by $\alpha''(\omega)$.

In Equation 2-37 one needs $\alpha'(\mathrm{i}\nu)$, which can be obtained by replacing ω^2 in Equation 2-49 by $(\mathrm{i}\omega)^2 = -(2\pi\nu)^2$. Nevertheless, it is noted that Equation 2-49 gives $\alpha'(\omega)$ as a discrete sum of contributions of differing ω_k, whereas the McLachlan Equation 2-37 contains a continuous frequency dependence. The latter approximation is valid, however, because over the relevant frequency range (usually 10^{14}–10^{16} s^{-1}) the steps between the various frequencies ω_k are so small that for practical purposes the sum may be replaced by an integral. On the other hand, as the zero-frequency state contributes only by a negligible amount, it is allowed in Equation 2-37 to take zero as the lower integration limit and the term $\omega\gamma_k$ in the denominator contributes significantly only for $\omega \approx \omega_k$.

Thus, with proper quantifications of the dielectric permittivity and polarizability of the medium as a function of frequency, it is possible to use the McLachlan formula to interpret dispersion forces. However, it should be kept in mind that in the interaction between two molecules there is no external field. The oscillating field of one molecule of a pair acts as the external field, polarizing the second. As to the forms of the equations this makes no difference but, in line with the second-order nature of Van der Waals forces, no dissipation of electrical energy can result, i.e. Van der Waals attractions cannot lead to a rise in temperature of the system.

Now the McLachlan formula has sufficiently been elucidated, and at this stage we can consider it for two one-electron molecules in a gas ($\varepsilon_3 = 1$) at frequencies not close to the resonance frequency, i.e. for the conditions for which the London equation applies. For the polarizability of the first molecule Equation 2-44 gives,

$$\alpha_1(\omega) = \frac{e^2}{m(\omega_1^2 - \omega^2)} \qquad (2\text{-}51)$$

It can be rewritten as, with the help of Equation 2-46,

$$\alpha_1(\omega) = \frac{\alpha_1(0)\omega_1^2}{(\omega_1^2 - \omega^2)} \qquad (2\text{-}52)$$

In the McLachlan formalism, however, imaginary frequencies are used, meaning that ω has to be replaced by $\mathrm{i}\omega$ and as a result we can write,

$$\alpha_1(\mathrm{i}\omega) = \frac{\alpha_1(0)\omega_1^2}{(\omega_1^2 + \omega^2)} \qquad (2\text{-}53)$$

In this case $\gamma = 0$, implying that α'' does not contribute to $\alpha(\mathrm{i}\omega)$.

For two unlike molecules 1 and 2, the McLachlan formula (2-37) now leads to,

$$\Phi_{\mathrm{M}} = -\frac{3h\alpha_1(0)\alpha_2(0)\omega_1^2\omega_2^2}{2(4\pi\varepsilon_0)^2\pi^2 r^6}\int_0^\infty \frac{\mathrm{d}\omega}{(\omega_1^2+\omega^2)(\omega_2^2+\omega^2)} \qquad (2\text{-}54)$$

It gives immediately, after performing the integration,

$$\Phi_{\mathrm{M}} = -\frac{3h\alpha_1(0)\alpha_2(0)\omega_1\omega_2}{4\pi(4\pi\varepsilon_0)^2 r^6(\omega_1+\omega_2)} \qquad (2\text{-}55)$$

which is identical to the London Equation 2-30 if we replace ω by $2\pi\nu$.

3 Interaction between macrobodies

There are two ways of describing Van der Waals interactions between colloidal particles and bigger units, which we collectively called macrobodies, i.e. the microscopic and the macroscopic approach.

The former one, also known as the Hamaker-De Boer theory /13, 14/, is an approximate treatment in which the total interaction energy is obtained by pair-wise summation of London-Van der Waals energies between all molecules of the interacting bodies. The quality of the underlying assumption of additivity of London-Van der Waals forces is however difficult to assess, since it is not so easy to quantify the influence of nearby molecules on the electric field emanating from given molecules. Neither can the effects of the medium and retardation be introduced rigorously in this theory. The best check is a comparison of the final results with those from the exact theory or with experiments. In this way, it has been found that usually the Hamaker-De Boer theory is correct within 10~30% with respect to the absolute magnitude and also it predicts the proper distance dependence in the limiting cases of short and long distances. As many practical systems are not particularly well defined and as it is much simpler to handle than the exact theory, the Hamaker-De Boer treatment remains an attractive alternative /1/.

The macroscopic approach, also known as the Lifshits theory /15, 16/, is more advanced and more abstract than the Hamaker-De Boer approximation. It considers interacting macrobodies as continuous media, and the origin of attraction does not differ from that between two atoms as in the London theory in that it is due to a correlation between fluctuations. Implementation of the Lifshits theory is, however, not so easy because for quantification the frequency dependences of macroscopic parameters such as dielectric permittivities of the medium are required, which are not always available.

3.1 The Hamaker-De Boer approximation

The main assumptions behind the Hamaker-De Boer theory /13, 14/ can be summarized as follows:

1. The molecular forces are pair-wise additive.
2. For mathematical convenience, the discrete sum over pairs is replaced by an integration.
3. The molecular forces are not screened by intervening molecules, i.e. they are not reduced by a factor of ε_3 squared as that described by the McLachlan formula.
4. Retardation is disregarded, i.e. the particle separation may not be too large.

To begin with, we will pay our attention on the treatment of macrobody interaction in a vacuum, where the Hamaker-De Boer approximation is expected, and proved, to be most accurate.

3.1.1 Attraction in a vacuum

Let us consider the case of a single molecule or atom close to a semi-infinite plate, as shown in Figure 3-1a.

The molecule of type 1 is situated in a vacuum, at a distance s from the plate. To our end, we can divide the plate into small rings of radius x and thickness dx in the xy-plane. The rings are located a distance z from the molecule 1, in the direction parallel to the plate-surface normal, and have a thickness dz in the respective direction.

The volume of each ring is thus $\mathrm{d}V = 2\pi x \mathrm{d}x \mathrm{d}z$ and the number of enclosed molecules of type 2 is $\mathrm{d}N = \rho_{\mathrm{N}2}\mathrm{d}V$, where $\rho_{\mathrm{N}2}$ is the number density of the molecules of the plate. Any molecules inside such ring is then located a distance r from the molecule outside the plate with $r^2 = x^2+z^2$.

According to the London Equation 2-30, we can write the energy of attraction between a molecule of type 1 and a molecule of type 2, at a distance r apart, simply as,

$$\Phi_{\mathrm{L}} = -\beta_{12} r^{-6} \tag{3-1}$$

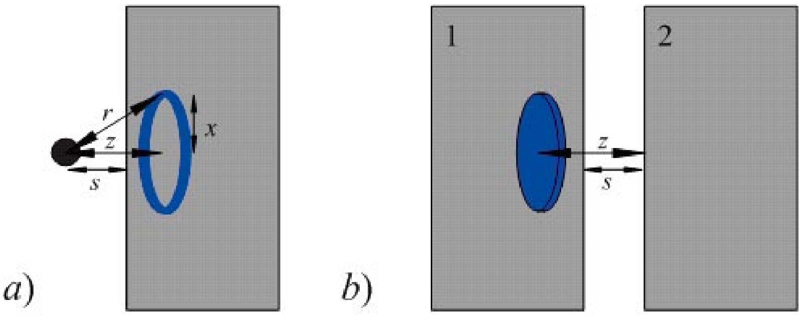

Figure 3-1. *Schematic illustration of calculating the Van der Waals interaction (a) between a molecule and a semi-infinite plate and (b) between two semi-infinite parallel plates.*

with the interaction parameter given by,

$$\beta_{12} = \frac{3h}{2}\frac{v_1 v_2}{v_1 + v_2}\frac{\alpha_1 \alpha_2}{(4\pi\varepsilon_0)^2} \tag{3-2}$$

where the subscript 12 serves as a reminder that the two molecules are unlike in general.

Thus, the total energy of attraction between the molecule and the ring reads,

$$\mathrm{d}G_{\mathrm{VdW}} = -\beta_{12}\rho_{\mathrm{N2}}\frac{2\pi x \mathrm{d}x \mathrm{d}z}{(x^2 + z^2)^3} \tag{3-3}$$

where we use G to denote the energy of attraction when a macrobody is involved, instead of Φ. The subscript VdW has been added to G to emphasize the fact that this energy is actually the Van der Waals contribution to the Gibbs energy of interaction.

Integration of this equation over the entire volume of the plate gives then the energy of Van der Waals attraction between the molecule and the semi-infinite plate as,

$$G_{\mathrm{VdW}} = -\int_s^\infty \int_0^\infty \beta_{12}\rho_{\mathrm{N2}}\frac{2\pi x \mathrm{d}x \mathrm{d}z}{(x^2 + z^2)^3} = -\frac{\pi\beta_{12}\rho_{\mathrm{N2}}}{6s^3} \tag{3-4}$$

This is an important equation. It gives the London-Van der Waals contribution to the adsorption energy which can now be computed as a function of the distance s. For very small s, however, this equation becomes less accurate because then the replacement of the sum by an integral is not a good approximation.

Now suppose that the molecule 1 is located inside a second semi-infinite plate with a number density of molecules of ρ_{N1}, as sketched in Figure 3-1b. We recognize that all molecules in a slice of the second plate a distance z from the first plate will be attracted toward the latter one with an energy given by Equation 3-4. If we position a volume element with unit area and thickness dz at this location in the second plate, which contains $\rho_{\mathrm{N1}}\mathrm{d}z$ molecules, the energy of attraction between this element and the first plate would be given by,

$$\mathrm{d}G_{\mathrm{a,\,VdW}} = -\pi\beta_{12}\rho_{\mathrm{N1}}\rho_{\mathrm{N2}}\frac{\mathrm{d}z}{6z^3} \tag{3-5}$$

where the subscript a serves as a reminder that we are dealing with an energy per unit area.

Integration of the above equation over values of z from the distance of closest approach s to infinite gives then the energy of attraction between a column of unit cross-section of plate 1 and the entire plate 2 as,

$$G_{\mathrm{a,\,VdW}} = -\frac{A_{12}}{12\pi \mathrm{s}^2} \tag{3-6}$$

where we have introduced the Hamaker constant,

$$A_{12} = \pi^2 \beta_{12} \rho_{\mathrm{N1}} \rho_{\mathrm{N2}} \tag{3-7}$$

For two semi-infinite parallel plates of the same material, the Hamaker constant becomes,

$$A_{11} = \pi^2 \beta_{11} \rho_{\mathrm{N1}}^2 \tag{3-8}$$

where the subscript 11 serves as a reminder that the two phases are of the same material.

According to the Berthelot principle /1/, for cases where the molecules of the two plates are not very different, we may have,

$$A_{12} \approx (A_{11} A_{22})^{1/2} \tag{3-9}$$

This expression says, essentially, that the attraction between two dissimilar bodies can be roughly given by the geometrical mean of the homogeneous attraction for the two species considered separately.

If the molecular properties of the materials under consideration are well known, we can use Equation 3-7 or 3-8 to calculate the Hamaker constant. Alternatively, it can be derived from the macroscopic theory or from experiments. The Hamaker constant has energy units, and at room temperature it typically lies in the range of 10^{-20}~10^{-19} J or 5~50 $k_{\mathrm{B}}T$ in a vacuum.

Equation 3-6 has two notable features. First, the attraction energy can be written as the product of a known material property and a geometrical factor. This rule remains valid for all geometries in the Hamaker-De Boer approximation and in the un-retarded limit of the macroscopic theory. Secondly, the s^2 term in the denominator is interesting. Mathematically, s^{-2} in Equation 3-6 as compared with r^{-6} in Equation 3-1 is due to the four directions over which we have integrated. The interaction between two macroscopic plates therefore has a much longer range than that between isolated molecules and this feature is responsible for the prominence of dispersion forces in colloidal phenomena.

With Equation 3-6 at hand, the force of attraction per unit area can be obtained directly from partial differentiation of the energy, with respect to the distance s; this leads to Van der Waals contribution to the disjoining pressure and for the case considered it givess,

$$\Pi_{\mathrm{VdW}} = -\frac{A_{12}}{6\pi s^3} \tag{3-10}$$

Likewise, Van der Waals energies of attraction have been calculated in the Hamaker-De Boer approximation for a host of geometries. These derivations involve no new physical features any more: for all cases under consideration we can generally write,

$$G_{\mathrm{VdW}} = -\beta_{12} \rho_{\mathrm{N1}} \rho_{\mathrm{N2}} \iint_{\text{1 and 2}} \frac{\mathrm{d}V_1 \mathrm{d}V_2}{r^6} \tag{3-11}$$

For the mathematically more complex cases of curved interfaces, however, there is a useful approximation, known after its originator as the Derjaguin approximation /17/, in which the curved surface is replaced by a stepped one.

To illustrate the Derjaguin approximation in a bit more detail, we now consider two spherical particles, as shown in Figure 3-2.

In this case, we approximate particle 1 by a stack of circular rings with planer surface of thickness dy and area dA. The total energy of attraction between the macrobodies is then considered to be build up of contributions of parallel rings where each pair contributes an amount,

$$\mathrm{d}G_{\mathrm{VdW}} = G_{\mathrm{a,VdW}} \mathrm{d}A \tag{3-12}$$

As the first factor at the r.h.s is an energy between a unit area of one macrobody and the complete other macrobody, given by Equation 3-6, the assumption is that elements adjust to the ring under consideration do not influence this ring. This approximation is good if the curvature is not strong, i.e. if the closest approach s is small with respect to the radii of curvature of the macrobodies.

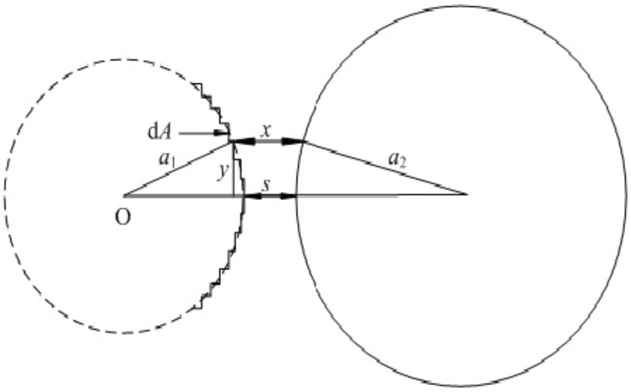

Figure 3-2. Illustrating the Derjaguin approximation for obtaining the energy of interaction between spherical particles from that for a flat surface.

From such energy per ring, the total energy of interaction is obtainable by integration over y (indicated in Figure 3-2). As the approximation is limited to short distances, the contributions of layers with large y are negligible, so that for convenience the integration may be carried out from $y = 0$ to $y = \infty$, i.e. we can write,

$$G_{\mathrm{VdW}} = \int_0^{\infty} G_{\mathrm{a,\,VdW}} \mathrm{d}A \tag{3-13}$$

After replacing $\mathrm{d}A = 2\pi y \mathrm{d}y$ and relating y to x, the Derjaguin formula for two spheres of radii a_1 and $a_2 >> s$ becomes,

$$G_{\mathrm{VdW}} = -\frac{2\pi a_1 a_2}{a_1 + a_2} \int_s^{\infty} G_{\mathrm{a,\,VdW}} \mathrm{d}x \tag{3-14}$$

Substituting Equation 3-6 and carrying out the integration then gives,

$$G_{\mathrm{VdW}} = -\frac{A_{12}}{6s} \frac{a_1 a_2}{a_1 + a_2} \tag{3-15}$$

For two spheres of equal radius of a, it becomes,

$$G_{\mathrm{VdW}} = -\frac{A_{12} a}{12s} \tag{3-16}$$

Once again, we stress that Equations 3-15 and 3-16 applies only to the limiting case where the radii of the spherical particles are much larger than the distance s.

For easy reference, we now summarize some equations obtained for what we think the most important scenarios in colloidal phenomena /1/. The meanings of the geometrical parameters are in each case given in a sketch. It is recalled that the equations are only valid for non-retarded Van der Waals forces.

(1) Molecule and semi-infinite plate (Figure 3-3)

$$G_{\mathrm{VdW}} = -\frac{\pi \beta_{12} \rho_{\mathrm{N2}}}{6s^3} \tag{3-17}$$

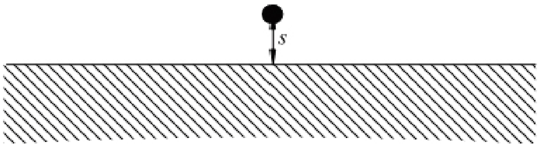

Figure 3-3.

(2) Two semi-infinite parallel plates (Figure 3-4)

$$G_{\text{a, VsW}} = -\frac{A_{12}}{12\pi s^2} \tag{3-18}$$

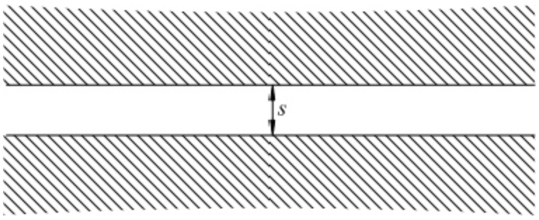

Figure 3-4.

(3) Two parallel slabs (Figure 3-5)

$$G_{\text{a, VdW}} = -\frac{A_{12}}{12\pi}\left[\frac{1}{s^2} + \frac{1}{(s+2\delta)^2} - \frac{2}{(s+\delta)^2}\right] \tag{3-19}$$

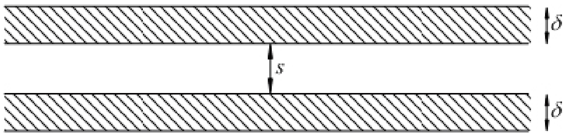

Figure 3-5.

(4) Rods and Laths (Figure 3-6)

For the limiting case of large distance ($s >> t, w$)

$$G_{\text{VdW}} = -\frac{3A_{12} l w^2 t^2}{8\pi s^5} \tag{3-20}$$

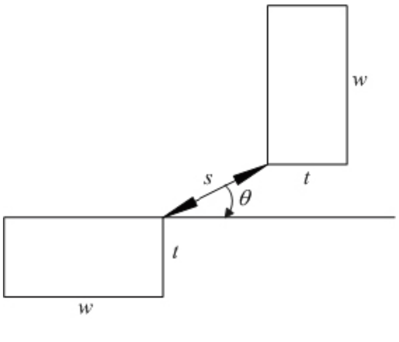

Figure 3-6. *Two parallels rods of length l. The figure gives a cross-section.*

For the limiting case of small distance ($s << t, w$), if θ is not zero,

$$G_{\text{VdW}} = -\frac{A_{12} l}{24\pi s}\frac{1-\sin^3\theta - \cos^3\theta}{\sin^2\theta\cos^2\theta} \tag{3-21}$$

For the limiting case of small distance ($s \ll t, w$), if θ is zero,

$$G_{\text{VdW}} = -\frac{A_{12} l w}{12 \pi s^2} \tag{3-22}$$

(5) Two cylinders (Figure 3-7)

For short distances and different radii,

$$G_{\text{VdW}} = -\frac{A_{12} l}{12\sqrt{2} s^{3/2}} \left(\frac{a_1 a_2}{a_1 + a_2} \right)^{1/2} \tag{3-23}$$

If $a_2 \gg a_1$, it becomes,

$$G_{\text{VdW}} = -\frac{A_{12} l a_1^{1/2}}{12\sqrt{2} s^{3/2}} \tag{3-24}$$

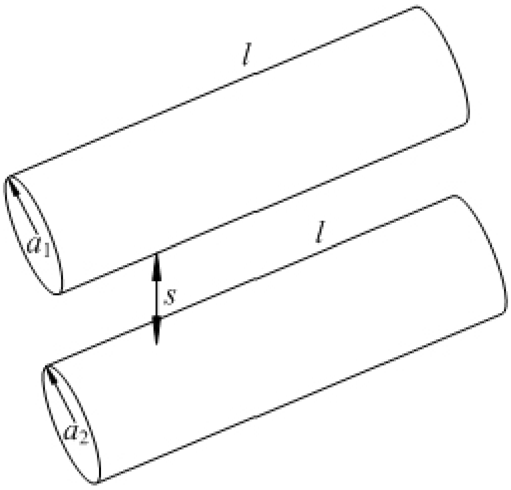

Figure 3-7.

3.1.2 Attraction in a medium

By invoking the Archimedes principle, a reasonable consideration of the influence of the intervening medium on the attraction between two macrobodies can be obtained. That is, if two macrobodies are brought from infinite distance to s in a medium, an equivalent amount of medium has to be transported the other way around. Thus, as illustrated in Figure 3-8, this process can be represented as a pseudo chemical reaction.

Initially, the two macrobodies (the geometry is immaterial for the argument that follows) 1 and 2 keep a large distance apart in medium 3, and therefore, the energy of attraction between 1 and 2 $G_{\text{VdW}} = 0$. At the end of the flocculation process, they are separated by a distance s.

The energy change of this pseudo chemical reaction (an exchange phenomenon) involves gains and losses. If we now write G_{VdW}, the energy of attraction between two types of particles generally as $-A_{ij}f(G)$, where $f(G)$ is an arbitrary but know function of geometry, the gains are $-A_{12}f(G)$, and $-A_{33}f(G)$, whereas the losses amount to $-A_{13}f(G)$, and $-A_{23}f(G)$. The energy change is then given by,

$$\Delta G_{\text{VdW}} = -A_{12(3)} f(G) = -(A_{12} - A_{13} - A_{23} + A_{33}) f(G) \tag{3-25}$$

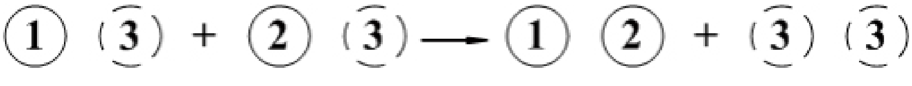

Figure 3-8. *The flocculation process as a pseudo chemical reaction. The solid lines indicate particles of the dispersed phase and the dashed lines satellite particles of the solvent.*

where $A_{12(3)}$ denotes the Hamaker constant for the interaction between two macrobodies 1 and 2 across the medium 3.

Thus, we may conclude that all the Hamaker-De Boer Equations derived for the energy of attraction in a vacuum would remain valid in a medium, provided the Hamaker constant A_{11} or A_{12} is replaced by,

$$A_{12(3)} = A_{12} - A_{13} - A_{23} + A_{33} \tag{3-26}$$

Application of the Berthelot principle, as given by Equation 3-9, would then lead to,

$$A_{12(3)} = \left(\sqrt{A_{11}} - \sqrt{A_{33}}\right)\left(\sqrt{A_{22}} - \sqrt{A_{33}}\right) \tag{3-27}$$

This gives rise to a number of interesting observations:

1. For homo-interaction (materials 1 and 2 are identical), the Hamaker constant $A_{11(3)}$ is always nonnegative, regardless of the relative magnitudes of A_{11} and A_{33}. Thus, two bodies of the same material in a medium invariably attract each other unless their Hamaker constant exactly matches that of the medium, in which case the force is zero.
2. The Hamaker constant $A_{11(3)}$ is always equal to $A_{33(1)}$. Hence, two water droplets in air attract each other equally strongly as two air bubbles of the same size in water.
3. For hetero-interaction (materials 1 and 2 are unlike), the Hamaker constant $A_{12(3)}$ can be negative if the A_{33} value for the medium is intermediate between A_{11} and A_{22} for the interacting bodies, i.e. $A_{11} < A_{33} < A_{22}$ or $A_{11} > A_{33} > A_{22}$. This implies that bodies of different material in a medium may repel each other. The repulsion is not due to the fact that the London forces are repulsive, but to the excess nature of $A_{11(3)}$: the excess attraction between 1 and 3 leads to the repulsion of 2 or the other way around.

It should be noted that these findings are qualitatively, but not quantitatively, supported by the macroscopic theory. The distance dependence at small s is found, so is the feature that in hetero-interaction the Van der Waals interaction may be repulsive. However, the equality of $A_{11(3)}$ and $A_{33(1)}$ is not entirely correct and the reason for the imperfection of the Hamaker-De Boer approximation must obviously be sought in the inaccurate account of the screening of London forces by the intervening medium.

3.1.3 Retarded attraction

In the framework of the Hamaker-De Boer approximation, retarded interaction energy can be obtained along the same lines as the non-retarded ones, except that Equation 2-31 is the starting equation instead of the London Equation 2-30.

Generally, we can write the energy of retarded attraction between a molecule of type 1 and a molecule of type 2, at a distance r apart in a vacuum, in a way similar to Equation 3-1, i.e.

$$\Phi_R = -\beta'_{12} r^{-7} \tag{3-28}$$

where β'_{12} is the retarded interaction parameter.

Consequently, the Hamaker-De Boer Equations for the non-retarded energy of attraction undergo two modifications: (1) the exponent in the denominator is increased by 1; (2) the Hamaker constant A_{12} is replaced by $6\pi B_{12}$, if we denote B_{12} as the retarded Hamaker constant for which the Berthelot principle also applies.

Thus the retarded interaction energy for two semi-infinite parallel plates can be given by, with the help of Equation 3-6,

$$G_{\text{a, VdW}} = -\frac{B_{12}}{2s^3} \tag{3-29}$$

and the force of attraction per unit area becomes,

$$\Pi_{\text{VdW}} = -\frac{3B_{12}}{2s^4} \tag{3-30}$$

In fact, for two perfectly conducting bodies (metals), it has been found by Casimir /18/ that,

$$\Pi_{\mathrm{VdW}} = -\frac{\pi hc}{480 s^4} \tag{3-31}$$

This gives, by comparison of Equations 3-30 and 3-31,

$$B_{12} = \frac{\pi hc}{720} \tag{3-32}$$

where it should be noted that the retarded Hamaker constant B_{12} does not have energy units, and typically it is of the order 10^{-28} J m.

For the transition region between non-retarded and retarded interaction no analytical expressions are available. The easiest procedure to obtain the energy of interaction, G_{VdW}, is by using Overbeek's approximate analytical expression (2-33), inserting it in Equation 2-32 and then carrying out the integrations needed. It may be interesting to note that Görner and Pich /18/ used this method to find the following alternative relation between the retarded and the Hamaker constant across a vacuum:

$$B_{12} \approx \frac{2.45\lambda}{40\pi^2} A_{12} \tag{3-33}$$

where λ is the wavelength of the electron vibration.

3.2 The Lifshits theory

Unlike the Hamaker-De Boer approach, the Lifshits theory considers interacting macro-bodies as continuous media, characterized by macroscopic parameters, especially their frequency-dependent (i.e. complex) dielectric permittivities.

Basically, the origin of attraction does not differ from that between two molecules or atoms as in the London theory in that it is due to a correlation between fluctuations. A macrobody contains many electrons, whose local densities can fluctuate. The amplitudes and frequencies of these fluctuations depend on the electron density and the strength of binding of the electron to the nuclei. These properties are reflected in the complex permittivity, as defined by Equation 2-38, a characteristic quantity of the substance. As a consequence of the spontaneous electronic fluctuations there is a fluctuating electro-magnetic field in and around the macrobody. The average field strength $\langle E \rangle$ of such a field is of course zero, but $\langle E^2 \rangle$ is finite. If two macrobodies come close enough for their fluctuation fields to overlap, a correlation between the two occurs, which can be shown to reduce the Gibbs energy; that is, it leads to attraction.

Quantitatively, based on the quantum electrodynamics of continuous media, the Lifshits theory elaborated a more general equation for the force between two macrobodies 1 and 2 in media 3 as /1/,

$$\begin{aligned}\Pi_{\mathrm{VdW}} = &-\frac{h}{4\pi^3 c^3}\int_0^\infty\!\!\int_1^\infty \xi^2\omega^3\varepsilon_3^{3/2}\left[\frac{(b_1+\xi)(b_2+\xi)}{(b_1-\xi)(b_2-\xi)}\exp\!\left(2\xi\omega s\varepsilon_3^{1/2}/c\right)-1\right]^{-1}\mathrm{d}\xi\mathrm{d}\omega\\ &-\frac{h}{4\pi^3 c^3}\int_0^\infty\!\!\int_1^\infty \xi^2\omega^3\varepsilon_3^{3/2}\left[\frac{(b_1+\xi\,\varepsilon_1/\varepsilon_3)(b_2+\xi\,\varepsilon_2/\varepsilon_3)}{(b_1-\xi\,\varepsilon_1/\varepsilon_3)(b_2-\xi\,\varepsilon_2/\varepsilon_3)}\exp\!\left(2\xi\omega s\varepsilon_3^{1/2}/c\right)-1\right]^{-1}\mathrm{d}\xi\mathrm{d}\omega\end{aligned} \tag{3-34}$$

with

$$b_1 = \left(\frac{\varepsilon_1}{\varepsilon_3} - 1 + \xi^2\right)^{1/2} \quad \text{and} \quad b_2 = \left(\frac{\varepsilon_2}{\varepsilon_3} - 1 + \xi^2\right)^{1/2} \tag{3-35}$$

where ξ is a dimensionless integration variable, running from 1 to ∞.

As expected, the interaction force requires integration over ω, the angular frequency of vibration of electrons. If $\varepsilon_1(\omega)$, $\varepsilon_2(\omega)$ and $\varepsilon_3(\omega)$ are known, this integration can be carried out. The distance dependence and hence the geometry is, however, given in an involved way: s occurs in the exponents, and the ensuing dependence $\Pi(s)$ is not simple.

Note that Equation 3-34 is an encompassing equation. It covers the media effect and applies both to short and long distances. It fails only when the distances become so short that the granularity of the media has to be taken into account. Once $\Pi(s)$ is found, the energy of Van der Waals attraction between two bodies can be obtained by integration.

The properties of Equation 3-34 become more transparent when some limiting cases are considered.

3.2.1 Non-retarded attraction

First, we look at the case of two semi-infinite parallel plates a short distance apart. As s in the exponent is now small, only high values of ξ contribute significantly. After taking the limits of the pre-exponential factors for $\xi >> 1$, $b_1 = b_2 = \xi$, changing the lower integration limit over ξ from unity to zero and introducing the dimensionless variable.

$$x = 2\xi\omega s\varepsilon_3^{1/2}/c \qquad (3\text{-}36)$$

Equation 3-34 reduces to,

$$\Pi_{\mathrm{VdW}} = -\frac{h}{32\pi^3 s^3}\int_0^\infty\int_0^\infty x^2\left[\frac{(\varepsilon_3+\varepsilon_1)(\varepsilon_3+\varepsilon_2)}{(\varepsilon_3-\varepsilon_1)(\varepsilon_3-\varepsilon_2)}e^x-1\right]^{-1}\mathrm{d}x\mathrm{d}\omega \qquad (3\text{-}37)$$

To a good approximation, the -1 may be neglected as compared to the term with e^x, after which the integration over x can be carried out analytically, leading to,

$$\Pi_{\mathrm{VdW}} = -\frac{h}{16\pi^3 s^3}\int_0^\infty\frac{(\varepsilon_3-\varepsilon_1)(\varepsilon_3-\varepsilon_2)}{(\varepsilon_3+\varepsilon_1)(\varepsilon_3+\varepsilon_2)}\mathrm{d}\omega \qquad (3\text{-}38)$$

The (Gibbs) energy of attraction is then obtained by integration over s. this gives,

$$G_{\mathrm{a,\,VdW}} = -\frac{h}{32\pi^3 s^2}\int_0^\infty\frac{(\varepsilon_3-\varepsilon_1)(\varepsilon_3-\varepsilon_2)}{(\varepsilon_3+\varepsilon_1)(\varepsilon_3+\varepsilon_2)}\mathrm{d}\omega \qquad (3\text{-}39)$$

which is the same result as in the Hamaker-De Boer theory, as given by Equation 3-6 with $A_{12(3)}$ instead of A_{12}, provided,

$$A_{12(3)} = -\frac{3h}{8\pi^2}\int_0^\infty\frac{(\varepsilon_3-\varepsilon_1)(\varepsilon_3-\varepsilon_2)}{(\varepsilon_3+\varepsilon_1)(\varepsilon_3+\varepsilon_2)}\mathrm{d}\omega \qquad (3\text{-}40)$$

Thus, for non-retarded forces, the Hamaker-De Boer approximation and this variant of the Lifshits theory give the same distance dependency. This is in fact the case for all other geometries, so that all the Hamaker-De Boer Equations we have obtained for short distances remain valid. However, the Hamaker constant now requires a macroscopic reinterpretation.

From Equation 3-40, we see that the Hamaker-De Boer approximation $A_{11(3)} = A_{33(1)}$ is corroborated, but in the more complete expression (3-34), it is no longer exact, although it is not easy to say by how much the two Hamaker constants differ.

3.2.2 Retarded attraction

Next, we consider the long distance case, again for planar symmetry. In this situation, $\varepsilon(\mathrm{i}\omega)$ may be replaced by its static value $\varepsilon(0)$, because the high-frequency waves are already damped out and we are now primarily dealing with long wavelengths or low frequencies. Thus, b_1 and b_2 may now be written as $b_1(0)$ and $b_2(0)$. After introducing the parameter x, as given by Equation 3-36, and eliminating ω, Equation 3-34 becomes,

$$\begin{aligned}\Pi_{\mathrm{VdW}} = &-\frac{hc}{64\pi^3 s^4\sqrt{\varepsilon_3(0)}}\int_0^\infty\int_1^\infty\frac{x^3}{\xi^2}\left\{\frac{[b_1(0)+\xi][b_2(0)+\xi]}{[b_1(0)-\xi][b_2(0)-\xi]}e^x-1\right\}^{-1}\mathrm{d}\xi\mathrm{d}x\\ &-\frac{hc}{64\pi^3 s^4\sqrt{\varepsilon_3(0)}}\int_0^\infty\int_1^\infty\frac{x^3}{\xi^2}\left\{\frac{[b_1(0)+\xi\varepsilon_1(0)][b_2(0)+\xi\varepsilon_2(0)]}{[b_1(0)-\xi\varepsilon_1(0)][b_2(0)-\xi\varepsilon_2(0)]}e^x-1\right\}^{-1}\mathrm{d}\xi\mathrm{d}x\end{aligned} \qquad (3\text{-}41)$$

It is seen that the force now decreases as s^{-4}, and by comparison with Equation 3-30 the retarded constant B_{12} can be obtained.

Thus, the Lifshits theory accounts automatically for retardation and, in the limiting cases for short and long distances, it corroborates the Hamaker-De Boer distance dependence.

For metals interacting across a vacuum, we have $\varepsilon_1(0) = \varepsilon_2(0) = \infty$, $\varepsilon_3 = 1$, and therefore, $b_1(0) = b_2(0) = \infty$. Equation 3-41 then simplifies to,

$$\Pi_{\mathrm{VdW}} = -\frac{hc}{32\pi^3 s^4}\int_0^\infty\int_1^\infty \frac{x^3}{\xi^2}(e^x-1)^{-1}\,\mathrm{d}\xi\,\mathrm{d}x = -\frac{\pi hc}{480 s^4} \tag{3-42}$$

This equation verifies Casimir's result, as given by Equation 3-31. For all metals the retarded Van der Waals force is the same: the equation does not contain material-specific parameters.

For the cases of intermediate distances and other than planar geometries, the Lifshits Equations have no analytical solutions and do not display the simple factoring into a material-dependent and a geometrical contribution as it was found in the Hamaker-De Boer approximation. The reason is that generally overlap takes place of contributions due to different frequency ranges. Hence, implementation of the Lifshits theory is not so easy, because integrations have to be carried out numerically and because complete dielectric spectra over the entire frequency range are not available for many substances.

This does not by any means exhaust the potential applications of the Lifshits theory. It can also be applied to a molecule interacting with a medium, leading to the Lifshits equivalent of Equation 3-4, or to obtain the force between two atoms or molecules.

Yet another interesting aspect of the Lifshits theory is that it can also set conditions for positive (repulsive) Van der Waals forces. Clearly, positive values of $\Pi(s)$ in the Lifshits Equation 3-34 are possible: it is seen that the sign is obtained by integration of differences between permittivities over the entire frequency range, i.e. the situation is more complicated than assumed in the Hamaker-De Boer approximation.

All of this underlines the generality of the Lifshits theory. However, a question remains, i.e. how to apply it in practice? To answer this question, we should realize that (1) not all parts of the dielectric spectrum are equally important and that (2) the approximation in Equation 3-34 of an integral over frequencies is not always realistic; in fact for a discrete spectrum it is better to relate ε to α using the Debye equation,

$$\frac{\varepsilon-1}{\varepsilon+2} = \frac{\rho_{\mathrm{N}}}{3\varepsilon_0}\left(\alpha + \frac{p^2}{3k_{\mathrm{B}}T}\right) \tag{3-43}$$

and interpret the latter according to Equations 2-44 and 2-45.

If crucial parts of the dielectric spectrum are well known and plausible estimates can be made of the less relevant parts, satisfactory results can be obtained without too much trouble. Examples of such computations are now becoming available in the literature. General rules about the parts of the spectrum that dominate cannot, however, be given: metals and water exhibit quite different dispersion.

Formally, for planar symmetry, the disjoining pressure can always be written as,

$$\Pi_{\mathrm{VdW}} = -\frac{A_{12}(s)}{6\pi s^3} \tag{3-44}$$

where $A_{12}(s)$, the Hamaker function, is distance generally dependent.

In the literature /1/, a number of approximate formulas for $A_{12}(s)$ are available. For most systems, at a short-distance of separation, $A_{12}(s)$ becomes independent of s and identical to the Hamaker constant.

4 Electric double layers

In general, electric double layers can be categorized into two kinds. One is the relaxed double layers, and the other one is the polarized double layers.

The relaxed double layers all form spontaneously by adsorption or desorption of charged species, and hence, the ensuing surface charge depends, according to some isotherm equations, on the concentration of the charge-determining species, i.e. on pAg for silver halide, pH for oxides, or on the concentration of anionic surfactants.

The polarized double layers are, however, generated by virtue of either an externally applied source, such as the mercury-solution interface, or isomorphic substitution of metal ions in the interior of the solid by ions of lower valency, such as the plates of clay minerals. Hence, the surface charge of the polarized double layers cannot be varied by changing the composition of the solution. Semiconductors with built-in vacancies or interstitial ions may also belong to this category, depending on the extent to which this charge can relax during an experiment.

In some cases, these two kinds of double layers may coexist to form a "mixed" double layer as typically encountered with clay minerals. The clay mineral platelet has on the edges a charge that is comparable with that on oxides, in that it is caused by adsorption or desorption of protons. At low pH, the edge surface charge is positive. However, the charge on the plates is negative and it has a very different origin, viz. isomorphic substitution in the interior of the solid (such as $Al^{3+} \rightarrow Mg^{2+}$, etc). This phenomenon has taken place during the genesis of the mineral and is caused by the limited availability of some species. The ensuing frozen-in shortage of positive space charge is felt, for a number of phenomena, as a negative surface charge that is manifested on the faces.

4.1 General description

The charge (either positive or negative) on the surface together with the compensating countercharge in the solution constitute an electrical double layer. The countercharge is, in fact, made up of two contributions; one from co-ions which have the same sign as the surface and the other one from counterions which have the opposite sign to the surface. Hence, a double layer contains surface-, co- and counterions.

4.1.1 The surface charge

As we mentioned previously, double layers for relaxed interfaces are solely created by preferential adsorption of certain types of ions. If it is known which of these ions are the surface ions (i.e. ions so strongly bound to the surface that the charge they impart may be identified as the surface charge), the surface charge density σ^0 or simply the "surface charge" can, in principle, be analytically determined. Immediately it is recognized that the decision to call ions "surface ions" is a bit arbitrary: some ions, binding moderately strongly, may be called "surface ions" by some and "specifically bound" by others. Thus, to avoid confusion, we shall restrict the notion of "surface ions" to species that are constituents of the particle or have a particularly high affinity to it. Often for such ions Nernst's law applies. For example, for colloidal AgI or AgI electrolytes Ag^+ and I^- will be defined as surface ions. Anionic surfactants, however strongly they may adsorb, are classified as specifically adsorbing. For oxides, H^+ and OH^- ions are identified as the surface ions but chemisorbing phosphate or cadmium ions are categorized as specifically adsorbing. In case of doubt careful specification is mandatory.

Surface ions may also be called "potential-determining" ions. This term is more common, but less precise, because it is not stated which potential is determined and therefore the measurability of that potential is subject to question.

For polarized interfaces, the surface charge is either fixed by the history of the particle (e.g. covalently bound sulphate groups on the surface of a latex particle are determined by the emulsion polymerization process) or it is the result of an applied potential (as in a dropping-mercury electrode). Also for these systems a variety of techniques are available to find the surface charge.

4.1.2 The countercharge

The countercharge of an electric double layer consists of an excess of counterions and a deficit of co-ions. The counterions feel the electrostatic attraction of the surface but at the same time tend to distribute themselves evenly over the solution, owing to thermal motion. The result is a compromise in which their concentration is high near the surface and decreases gradually till the bulk value is reached at large distance. The co-ions are, on the other hand, repelled from the surface; their concentration is very low near the surface and increases gradually until the bulk value is again reached.

If the countercharge is distributed as described above, without any specifically binding to the surface, the double layer is called purely diffuse. Otherwise additionally a thin layer, called the Stern layer, adjacent to the surface would be found with specifically adsorbing ions. Thus, a double layer can be divided generally into three parts: the surface, the Stern layer and the diffuse layer. Correspondingly, the charges are termed as the surface charge σ^0, the specifically adsorbed charge σ^s and the diffuse charge σ^d, respectively.

Often, one speaks of specific adsorption when part of the countercharge is bound to the surface by non-electrostatic forces. The term derives from the fact that non-electrostatic binding energies typically depend on the nature of the ion, say on its radius, whereas for purely Coulombic interactions between point charges, as is the case in diffuse layers, usually the interaction is generic: identical for all ions of the same valency.

In addition, for the diffuse part of an electrical double layer, the excess charge attributed by cations,

$$\sigma_+^d = \sum\nolimits_j z_{j+} F \Gamma_{j+} \tag{4-1}$$

and that by anions,

$$\sigma_-^d = \sum\nolimits_k z_{k-} F \Gamma_{k-} \tag{4-2}$$

are called the ionic components of charge, because both of them are parts of the diffuse charge, i.e.

$$\sigma_+^d + \sigma_-^d = \sigma^d \tag{4-3}$$

For a positive surface, the ionic components of charge are both negative, whereas for a negative surface, they are both positive.

4.1.3 The Gibbs energy

The concept of the Gibbs or Helmholtz energy of electrical double layers plays a central role in colloid science. It is, for instance, needed in describing the properties of poly-electrolytes, dissociated mono-layers and the interaction of colloids.

By definition we can write, for flat interfaces at constant pressure,

$$\mathrm{d}G^\sigma = -S^\sigma \mathrm{d}T - A\mathrm{d}\gamma + \sum\nolimits_i \mu_i \mathrm{d}n_i^\sigma \tag{4-4}$$

and

$$\mathrm{d}F^\sigma = -S^\sigma \mathrm{d}T + \gamma \mathrm{d}A + \sum\nolimits_i \mu_i \mathrm{d}n_i^\sigma \tag{4-5}$$

where G and F are the Gibbs and Helmholtz energy, respectively, with the superscript σ specifying for the interfaces, A and γ denote the interfacial area and the surface tension, respectively, S is the entropy, T is the absolute temperature, whereas n_i and μ_i are the number of moles and the chemical potential of the species *i* in the interface.

To our end, we may further express both energies explicitly in terms of the electrical and non-electrostatic (chemical) contributions. For the Gibbs energy, this gives,

$$\Delta G^\sigma = \Delta G^\sigma\ (\text{el.}) + \Delta G^\sigma\ (\text{nonel.}) \tag{4-6}$$

In principle the electrical contribution can be obtained by some reversible isothermal charging processes, depending on the nature of the system and on the rigour one wants to obtain. Provided that during the charging no density changes take place (i.e. absence of electrostriction), the Gibbs and Helmholtz energies would be identical, and so would be enthalpies and entropies.

The charging runs, however, differently for relaxed and polarized interfaces. We shall discuss the former category in some detail because it is more typical and because the uncharged (reference) state is physically better imaginable.

Regarding the charging process, there are two options, each having its merits and draw-backs, some of which appear only in later stages.

The first approach is similar to the Debye-Hückel type of charging: at the onset all ions are uncharged and there is no adsorption; infinitesimal amounts of charge are then transported from some types of ions to others, allowing the systems to adjust or regulate its configuration after each step. During this process, the adsorption of some of the ions (the surface ions, also called the potential-determining ions) will change by an amount determined by their chemical affinities. The surface and the solution side of the double layer are in this way simultaneously charged.

The alternative starts with the situation that uncharged colloidal particle are brought into an infinitely large solution, containing surface ions, specifically adsorbing as well as indifferent ions. The system is not in equilibrium, which poses a problem of principle because we must carry out some reversible charging process. Surface ions will adsorb because of chemical forces together with any specific adsorption; this is the very driving force for double layer formation: ΔG^{σ}(nonel.) < 0. Concomitantly an electrical double layer forms, for which ΔG^{σ}(el.) > 0 because ions of like sign have to be brought into close proximity. Relaxed double layers never form on the basis of purely electrical interactions.

The balance between ΔG^{σ}(nonel.) and ΔG^{σ}(el.) changes during the charging process. Chemical interactions are short range. Hence, if taken per unit of added adsorbed charge, $\partial\Delta G^{\sigma}(\text{nonel.})/\partial\Gamma_{\text{i}}$ is essentially independent of Γ_{i}. In this section we assume this independence to be the case in order to emphasize the principles. This situation arises for most double layers on homogeneous surfaces at not too high surface charge and also applies to double layers formed by specific adsorption of ionic surfactants, as long as lateral interaction is negligible. On the other hand, $\partial\Delta G^{\sigma}(\text{el.})/\partial\Gamma_{\text{i}}$ is not constant; it increases with charging because the potentials increase. In fact, the charging continues spontaneously until $\partial\Delta G^{\sigma}(\text{el.})/\partial\Gamma_{\text{i}} = \partial\Delta G^{\sigma}(\text{nonel.})/\partial\Gamma_{\text{i}}$. Integrated over the entire process, ΔG^{σ} must be negative because the double layer forms spontaneously for relaxed double layers.

Specifically, for a simple double layer in which all surface ions adsorb in the same plane without any specific adsorption, we can write the electrical contribution to the Gibbs energy per unit area as,

$$\Delta G_{\text{a}}^{\sigma}(\text{el.}) = \int_{0}^{\sigma^{0}} \psi^{0'} \mathrm{d}\sigma^{0'} \tag{4-7}$$

where σ^0 and ψ^0 are the surface charge density and surface potential, respectively. The primes indicate the variable values when the double layer is reversibly charged from zero to its final charge σ^0 with a final potential of ψ^0.

In the above equation, we do not add a contribution due to the secondary rearrangement of charges in the solution side of the double layer because, by virtue of the continuous equilibrium with the solution, this rearrangement involves no change in Gibbs energy. In further detail, the work gained by transporting, say, a counterion from the solution to a position in the double layer where the potential is $\psi(x)$ just equals the corresponding loss of entropy and therefore the resulting ionic distribution follows the Boltzmann's law /1/.

Now consider the chemical contribution. Recall that we assumed $\partial\Delta G^{\sigma}(\text{nonel.})/\partial\Gamma_{\text{i}}$ to be constant for each chemically adsorbing species *i*. At any plane in the double layer where chemical adsorption takes place, this process continues until eventually the decrement in ΔG^{σ}(nonel.) is just equal and opposite to the increment of ΔG^{σ}(el.). Mathematically, when adsorbing the last ion, $\mathrm{d}\Delta G^{\sigma}(\text{nonel.}) = \text{const} = -\mathrm{d}\Delta G^{\sigma}(\text{el., final step}) = -\psi^0\mathrm{d}\sigma^0$. Hence, we may integrate and write the chemical contribution to the Gibbs energy per unit area as,

$$\Delta G_{\text{a}}^{\sigma}(\text{nonel.}) = -\psi^{0}\sigma^{0} \tag{4-8}$$

Combination of Equations 4-6, 4-7 and 4-8 immediately gives,

$$\Delta G_{\text{a}}^{\sigma} = -\int_{0}^{\psi^{0}} \sigma^{0'} \mathrm{d}\psi^{0'} \tag{4-9}$$

which is always negative.

Likewise, in the more complicated case where not only surface ions adsorb but specific adsorption of ions of type *j* also takes place, we have,

$$\Delta G_{\mathrm{a}}^{\sigma}(\mathrm{el.}) = \int_{0}^{\sigma^{0}} \psi^{0'} \mathrm{d}\sigma^{0'} + \sum\nolimits_{\mathrm{j}} \int_{0}^{\sigma^{\mathrm{j}}} \psi^{\mathrm{j'}} \mathrm{d}\sigma^{\mathrm{j'}} \tag{4-10}$$

and

$$\Delta G_{\mathrm{a}}^{\sigma} = -\int_{0}^{\psi^{0}} \sigma^{0'} \mathrm{d}\psi^{0'} - \sum\nolimits_{\mathrm{j}} \int_{0}^{\psi^{\mathrm{j}}} \sigma^{\mathrm{j'}} \mathrm{d}\psi^{\mathrm{j'}} \tag{4-11}$$

where ψ^{j} is the potential of the inner Helmholtz plane.

Thus, Gibbs energies can be computed if the charges are known as functions of the potentials. The function $\sigma^{0}(\psi^{0})$ is obtainable from colloid titrations provided Nernst's law applies. Often σ^{j} can be determined analytically, but ψ^{j} may offer problems. Under certain conditions it may be approximated by the electrokinetic potential ζ. Alternatively, the Gibbs energy is obtainable through double-layer models, e.g. Gouy-Chapman theory gives explicit equations for $\sigma^{0}(\psi^{0})$ that can be integrated.

Note also that in both Equations 4-9 and 4-11 the diffuse part of the double layer does not contribute to the Gibbs energy, because no non-electrostatic interactions are involved: in this part changes in electrochemical potential due to changes in concentration are balanced exactly by changes in potential, according to Boltzmann's law /1/.

When the surfaces are heterogeneous, however, these expressions must be replaced by more complicated ones. In the relatively simple situation that it consists of independent patches, each small enough to be homogeneous, Equations 4-7 and 4-9 or 4-10 and 4-11 may be applied to each patch and all contributions added.

4.2 The Poisson-Boltzmann model

The counterions of a diffuse double layer are subjected to two opposing tendencies. Electrostatic forces attract them to the charged surface, whereas diffusion tends to bring them from the surface toward the bulk solution, where their concentration is smaller.

Simultaneously, the co-ions are repelled by the surface, and back-diffusion from the bulk solution toward the surface counteracts the electric repulsion.

When equilibrium is established in the double layer, the average local concentration of ions can be described as a function of the average electric potential, ψ, according to Boltzmann's law,

$$c_{\mathrm{j}} = c_{\mathrm{j}\infty} \exp\left(-\frac{z_{\mathrm{j}} F \psi}{RT}\right) \tag{4-12}$$

where c_{j} is the concentration of ions of type *j* per unit volume near the surface, and $c_{\mathrm{j}\infty}$ is the concentration far from the surface, i.e. the bulk concentration. The valence number z_{j} is either a positive or negative integer.

The electric field thus formed can be quantified properly, without proof, by Poisson's equation,

$$\nabla \cdot (\varepsilon \nabla \psi) = -\frac{\rho}{\varepsilon_{0}} \tag{4-13}$$

with the space charge density given by,

$$\rho = F \sum\nolimits_{\mathrm{j}} z_{\mathrm{j}} c_{\mathrm{j}} \tag{4-14}$$

where the sum over *j* covers all ionic species present.

For constant ε (the relative dielectric permittivity of the solution), Poisson's equation reduces to,

$$\nabla^2\psi = -\frac{\rho}{\varepsilon_0\varepsilon} \tag{4-15}$$

Thus, combination of Equations 4-12, 4-14 and 4-15 gives the Poisson-Boltzmann (PB) Equation, for the diffuse part of the double layer, as,

$$\nabla^2\psi = -\frac{F}{\varepsilon_0\varepsilon}\sum\nolimits_{\mathrm{j}} z_{\mathrm{j}} c_{\mathrm{j}\infty} \exp\left(-\frac{z_{\mathrm{j}}F\psi}{RT}\right) \tag{4-16}$$

At this point we should understand that the PB Equation was developed firmly based on the following premises, viz.

1. The ions are point charges.
2. The ionic adsorption energy is purely electrostatic.
3. The average electrostatic potential is identified with the potential of mean force.
4. The solvent is primitive, i.e. a structureless continuum, affecting the distribution only through its macroscopic dielectric permittivity ε_r, for which the bulk value is taken.

Note that the Poisson Equation 4-15, supplemented by Equation 4-14, implies that the potentials associated with various charges combine in an additive manner. The Boltzmann Equation 4-12 involves, however, an exponential relationship between the charges and the potentials. Thus, a fundamental inconsistency is introduced when Equations 4-12 and 4-15 are combined via Equation 4-14. As a result, the Poisson-Boltzmann Equation 4-16 does not have an explicit general solution anyhow and must be solved numerically. Only for certain limiting cases can it be solved analytically, and these involve approximations which at the same time overcome the objection just stated.

Now introducing a normalized dimensionless potential,

$$y = \frac{F\psi}{RT} \tag{4-17}$$

the PB Equation 4-16 may be rewritten as,

$$\nabla^2 y = -\frac{F^2}{\varepsilon_0\varepsilon RT}\sum\nolimits_{\mathrm{j}} z_{\mathrm{j}} c_{\mathrm{j}\infty} \exp(-z_{\mathrm{j}}y) \tag{4-18}$$

For flat geometry, the Laplace operator becomes,

$$\nabla^2 y = \frac{\mathrm{d}^2 y}{\mathrm{d}x^2} \tag{4-19}$$

and then, Equation 4-18 reduces to,

$$\frac{\mathrm{d}^2 y}{\mathrm{d}x^2} = -\frac{F^2}{\varepsilon_0\varepsilon RT}\sum\nolimits_{\mathrm{j}} z_{\mathrm{j}} c_{\mathrm{j}\infty} \exp(-z_{\mathrm{j}}y) \tag{4-20}$$

with the distance x being counted from the surface if the double layer is purely diffuse or from the outer Helmholtz plane.

This equation can be integrated after multiplying both sides with 2(dy/dx). As

$$2\frac{\mathrm{d}y}{\mathrm{d}x}\frac{\mathrm{d}^2 y}{\mathrm{d}x^2} = \frac{\mathrm{d}}{\mathrm{d}x}\left[\left(\frac{\mathrm{d}y}{\mathrm{d}x}\right)^2\right] \tag{4-21}$$

and

$$2\frac{\mathrm{d}y}{\mathrm{d}x}\sum\nolimits_{\mathrm{j}} z_{\mathrm{j}} c_{\mathrm{j}\infty} \exp(-z_{\mathrm{j}}y) = -2\frac{\mathrm{d}}{\mathrm{d}x}\left[\sum\nolimits_{\mathrm{j}} c_{\mathrm{j}\infty} \exp(-z_{\mathrm{j}}y)\right] \tag{4-22}$$

the equation can be integrated to give,

$$\left(\frac{\mathrm{d}y}{\mathrm{d}x}\right)^2=\frac{2F^2}{\varepsilon_0\varepsilon RT}\left[\sum_{\mathrm{j}} c_{\mathrm{j}\infty}\exp(-z_{\mathrm{j}}y)+C\right] \tag{4-23}$$

where C is the integration constant, and it can be found from the boundary condition that at large distance from the surface $\mathrm{d}y/\mathrm{d}x \to 0$ and $y \to 0$; this gives,

$$C=-\sum_{\mathrm{j}} c_{\mathrm{j}\infty} \tag{4-24}$$

Hence,

$$\frac{\mathrm{d}y}{\mathrm{d}x}=-(\mathrm{sign}y)\left(\frac{2F^2}{\varepsilon_0\varepsilon RT}\right)^{1/2}\left[\sum_{\mathrm{j}} c_{\mathrm{j}\infty}\exp(-z_{\mathrm{j}}y)-\sum_{\mathrm{j}} c_{\mathrm{j}\infty}\right]^{1/2} \tag{4-25}$$

Although this equation becomes analytically unsolvable for most systems, it can be used to evaluate some important quantities. In the following, we shall restrict ourselves to flat surfaces and work mainly on Equations 4-20 and 4-25, discussing about the basic properties of the diffuse double layers for different cases.

4.2.1 Electrolyte mixture and the Debye-Hückel approximation

When dealing with electrolyte mixtures, the ionic concentrations $c_{\mathrm{j}\infty}$ can be rewritten in terms of concentrations of electroneutral electrolytes, $c_{\mathrm{i}\infty}$. Suppose one molecule of electrolyte i dissociates into $\nu_{\mathrm{i}+}$ cations of valency $z_{\mathrm{i}+}$, and $\nu_{\mathrm{i}-}$ anions of valency $z_{\mathrm{i}-}$, Equation 4-25 becomes generally,

$$\frac{\mathrm{d}y}{\mathrm{d}x}=-(\mathrm{sign}y)\left(\frac{2F^2}{\varepsilon_0\varepsilon RT}\right)^{1/2}\left[\sum_{\mathrm{i}} c_{\mathrm{i}\infty}\nu_{\mathrm{i}+}\exp(-z_{\mathrm{i}+}y)+\sum_{\mathrm{i}} c_{\mathrm{i}\infty}\nu_{\mathrm{i}-}\exp(-z_{\mathrm{i}-}y)-\sum_{\mathrm{i}} c_{\mathrm{i}\infty}(\nu_{\mathrm{i}+}+\nu_{\mathrm{i}-})\right]^{1/2} \tag{4-26}$$

When the electrolytes possess common ions, some terms may be grouped together.

The electric field strength

For flat surfaces, the electric field strength in a diffuse double layer is given by,

$$E(x)=-\frac{\mathrm{d}\psi}{\mathrm{d}x} \tag{4-27}$$

and thus, from Equation 4-26, we can immediately write,

$$E(x)=(\mathrm{sign}y)\left(\frac{2RT}{\varepsilon_0\varepsilon}\right)^{1/2}\left[\sum_{\mathrm{i}} c_{\mathrm{i}\infty}\nu_{\mathrm{i}+}\exp(-z_{\mathrm{i}+}y)+\sum_{\mathrm{i}} c_{\mathrm{i}\infty}\nu_{\mathrm{i}-}\exp(-z_{\mathrm{i}-}y)-\sum_{\mathrm{i}} c_{\mathrm{i}\infty}(\nu_{\mathrm{i}+}+\nu_{\mathrm{i}-})\right]^{1/2} \tag{4-28}$$

The diffuse charge

Using Gauss' law, the diffuse charge can be related to the field strength such that,

$$\sigma^{\mathrm{d}}=-\varepsilon_0\varepsilon E\big|_{x=0} \tag{4-29}$$

Hence, Equation 4-28 immediately gives,

$$\sigma^{\mathrm{d}}=-\left(\mathrm{sign}y^{\mathrm{d}}\right)\left(2\varepsilon_0\varepsilon RT\right)^{1/2}\left[\sum_{\mathrm{i}} c_{\mathrm{i}\infty}\nu_{\mathrm{i}+}\exp\left(-z_{\mathrm{i}+}y^{\mathrm{d}}\right)+\sum_{\mathrm{i}} c_{\mathrm{i}\infty}\nu_{\mathrm{i}-}\exp\left(-z_{\mathrm{i}-}y^{\mathrm{d}}\right)-\sum_{\mathrm{i}} c_{\mathrm{i}\infty}(\nu_{\mathrm{i}+}+\nu_{\mathrm{i}-})\right]^{1/2} \tag{4-30}$$

where y^{d} is the dimensionless potential of the diffuse part, i.e. the potential y at $x = 0$, either at the surface if the double layer is purely diffuse or at the outer Helmholtz plane.

The differential capacitance

The differential capacitance of a diffuse double layer is defined as,

$$C=\frac{\mathrm{d}\sigma^0}{\mathrm{d}\psi^0} \tag{4-31}$$

where σ^0 and ψ^0 denote the surface charge and surface potential, respectively.

As a whole, electric double layers are always electroneutral. Thus, if the countercharge is purely diffuse, we have,

$$\sigma^0 + \sigma^{\mathrm{d}} = 0 \tag{4-32}$$

and

$$\psi^0 = \psi^{\mathrm{d}} \tag{4-33}$$

This gives,

$$C^{\mathrm{d}} = -\frac{\mathrm{d}\sigma^{\mathrm{d}}}{\mathrm{d}\psi^{\mathrm{d}}} \tag{4-34}$$

where the superscript d has been added to C as a reminder that this applies for a purely diffuse double layer or, more generally, the diffuse part of the double layer.

As a result, differentiating Equation 4-30 with respect to ψ^{d} immediately yields,

$$C^{\mathrm{d}} = \left(\frac{\varepsilon_0 \varepsilon c F^2}{2RT}\right)^{1/2} \frac{\left|\sum_{\mathrm{i}} c_{\mathrm{i}\infty} v_{\mathrm{i+}} z_{\mathrm{i+}} \exp\left(-z_{\mathrm{i+}} y^{\mathrm{d}}\right) + \sum_{\mathrm{i}} c_{\mathrm{i}\infty} v_{\mathrm{i-}} z_{\mathrm{i-}} \exp\left(-z_{\mathrm{i-}} y^{\mathrm{d}}\right)\right|}{\left[\sum_{\mathrm{i}} c_{\mathrm{i}\infty} v_{\mathrm{i+}} \exp\left(-z_{\mathrm{i+}} y^{\mathrm{d}}\right) + \sum_{\mathrm{i}} c_{\mathrm{i}\infty} v_{\mathrm{i-}} \exp\left(-z_{\mathrm{i-}} y^{\mathrm{d}}\right) - \sum_{\mathrm{i}} c_{\mathrm{i}\infty}\left(v_{\mathrm{i+}} + v_{\mathrm{i-}}\right)\right]^{1/2}} \tag{4-35}$$

It indicates that, in the plot of C^{d} *vs.* y^{d}, the capacitance minimum does not coincide with the zero point of the diffuse potential.

The potential distribution

Generally, no analytical solution can be given for $y(x)$ for electrolyte mixtures. When the Debye-Hückel approximation holds, however, the PB equation can be linearized, and as a result it becomes analytically solvable.

In the limit of low potentials, the exponentials in Equation 4-20 can be expanded as a power series. If only the zeroth- and first-order terms are retained, the equation becomes,

$$\frac{\mathrm{d}^2 y}{\mathrm{d}x^2} = \kappa^2 y \tag{4-36}$$

with the reciprocal Debye length κ given by,

$$\kappa^2 = \frac{F^2 \sum_{\mathrm{j}} c_{\mathrm{j}\infty} z_{\mathrm{j}}^2}{\varepsilon_0 \varepsilon RT} = \frac{2IF^2}{\varepsilon_0 \varepsilon RT} \tag{4-37}$$

where I is the ionic strength of the bulk solution and noticeably it has a unit of mol m^{-3} here.

Integration of Equation 4-36, following the same procedure from Equation 4-20 to Equation 4-25, yields,

$$\frac{\mathrm{d}y}{\mathrm{d}x} = -\kappa y \tag{4-38}$$

This equation can be integrated once again, using the boundary condition that $y = y^{\mathrm{d}}$ at $x = 0$, to give the analytical solution of the potential distribution in a diffuse double layer,

$$y = y^{\mathrm{d}} \exp(-\kappa x) \tag{4-39}$$

Making y explicit, by Equation 4-17, we obtain,

$$\psi = \psi^{\mathrm{d}} \exp(-\kappa x) \tag{4-40}$$

Thus, at low potentials, the absolute value of the electrostatic potential in a flat diffuse double layer drops exponentially with distance, reducing to ψ^{d}/e over a distance κ^{-1}.

Although the Debye-Hückel approximation is strictly applicable only in the case of low potentials, this analysis reveals some features of the diffuse double layer that are general and of great importance as far as stability with respect to flocculation of dispersions and electrokinetic phenomena are concerned.

1. The distance away from the surface that an electrostatic potential persists may be comparable to the dimensions of colloidal particles themselves.
2. The distance over which significant potentials exist decreases with increasing electrolyte concentration and the valence of the ions in the bulk solution. The valence plays a dominant role as compared to the concentration.
3. The indifferent electrolytes not only compress the double layer but also reduce the potential of the diffuse part of the double layer.

More importantly, in this limiting case, the basic quantities that characterize the diffuse double layers would become physically better imaginable.

The electric field strength

With the help of Equations 4-27 and 4-38, we can immediately write the electric field strength in a diffuse double layer as,

$$E = \kappa\psi \qquad (4\text{-}41)$$

where the potential ψ, as given by Equation 4-40, is a function of x.

The diffuse charge

Following Gauss' law, as described by Equation 4-29, the diffuse charge can be found directly from Equation 4-41, to give,

$$\sigma^{\mathrm{d}} = -\varepsilon_0\varepsilon\kappa\psi^{\mathrm{d}} = -\frac{\varepsilon_0\varepsilon\kappa RT}{F}y^{\mathrm{d}} \qquad (4\text{-}42)$$

and the inverse of this expression yields,

$$y^{\mathrm{d}} = -\frac{F\sigma^{\mathrm{d}}}{\varepsilon_0\varepsilon\kappa RT} \qquad (4\text{-}43)$$

The differential capacitance

By differentiating Equation 4-42 with respect to ψ^{d}, we can obtain the differential capacitance of a diffuse double layer as,

$$C^{\mathrm{d}} = \varepsilon_0\varepsilon\kappa \qquad (4\text{-}44)$$

This result shows that a purely diffuse double layer at low potentials behaves just like a parallel plate capacitor in which the separation between the plates is given by κ^{-1}. This explains why κ^{-1} is also called the double layer thickness. It is important to remember, however, that the actual distribution of counterions in the diffuse double layer is diffuse, as shown later, and approaches the unperturbed bulk value only at large distance from the surface.

The Gibbs energy

With the help of Equations 4-9 and 4-42, the Gibbs energy per unit area can now be computed for a purely diffuse double layer; it gives,

$$\Delta G_{\mathrm{a}}^{\sigma} = -\frac{\varepsilon_0\varepsilon\kappa}{2}\left(\psi^{\mathrm{d}}\right)^2 \qquad (4\text{-}45)$$

Using the dimensionless potential y^{d}, it can also be written as,

$$\Delta G_{\mathrm{a}}^{\sigma} = -\frac{\varepsilon_0 \varepsilon \kappa}{2}\left(\frac{RTy^{\mathrm{d}}}{F}\right)^2 \tag{4-46}$$

or, by Equation 4-42, we have,

$$\Delta G_{\mathrm{a}}^{\sigma} = \frac{\sigma^{\mathrm{d}}\psi^{\mathrm{d}}}{2} = \frac{RT}{2F}\sigma^{\mathrm{d}} y^{\mathrm{d}} \tag{4-47}$$

4.2.2 Single electrolyte and the Gouy-Chapman theory

If only one electrolyte is involved in the bulk solution, the PB equation can be written in a bit more handy form.

To start with, we consider the electrolyte to be asymmetrical. Suppose one molecule of the electrolyte dissociates into v_+ cations of valency z_+, and v_- anions of valency z_-, the cation and anion concentrations are then given by,

$$c_+ = v_+ c \qquad \text{and} \qquad c_- = v_- c \tag{4-48}$$

where we have used c to stand for the bulk concentration of the electroneutral electrolyte, instead of c_∞.

Thus, Equation 4-20 becomes,

$$\frac{\mathrm{d}^2 y}{\mathrm{d}x^2} = -\frac{F^2}{\varepsilon_0 \varepsilon RT}\left[z_+ c_+ \exp(-z_+ y) + z_- c_- \exp(-z_- y)\right] \tag{4-49}$$

and correspondingly Equation 4-25 reduces to,

$$\frac{\mathrm{d}y}{\mathrm{d}x} = -(\mathrm{sign}y)\left(\frac{2cF^2}{\varepsilon_0 \varepsilon RT}\right)^{1/2}\left[v_+ \exp(-z_+ y) + v_- \exp(-z_- y) - v_+ - v_-\right]^{1/2} \tag{4-50}$$

The electric field strength

From Equation 4-50, the electric field strength in a diffuse double layer is immediately found as,

$$E = (\mathrm{sign}y)\left(\frac{2cRT}{\varepsilon_0 \varepsilon}\right)^{1/2}\left[v_+ \exp(-z_+ y) + v_- \exp(-z_- y) - v_+ - v_-\right]^{1/2} \tag{4-51}$$

The diffuse charge

With the help of Equation 4-51, the diffuse charge can be determined as,

$$\sigma^{\mathrm{d}} = -(\mathrm{sign}y^{\mathrm{d}})(2\varepsilon_0 \varepsilon cRT)^{1/2}\left[v_+ \exp(-z_+ y) + v_- \exp(-z_- y) - v_+ - v_-\right]^{1/2} \tag{4-52}$$

The differential capacitance

When an asymmetrical electrolyte is involved, the differential capacitance of a diffuse double layer is found directly from differentiation of Equation 4-52 with respect to ψ^{d}, to give,

$$C^{\mathrm{d}} = \left(\frac{\varepsilon_0 \varepsilon cF^2}{2RT}\right)^{1/2}\frac{\left|v_+ z_+ \exp(-z_+ y^{\mathrm{d}}) + v_- z_- \exp(-z_- y^{\mathrm{d}})\right|}{\left[v_+ \exp(-z_+ y^{\mathrm{d}}) + v_- \exp(-z_- y^{\mathrm{d}}) - v_+ - v_-\right]^{1/2}} \tag{4-53}$$

Because of electroneutrality, we have,

$$z_+ c_+ = -z_- c_- \qquad \text{and} \qquad z_+ v_+ = -z_- v_- \tag{4-54}$$

Subsequently, we can rewrite Equation 4-53 as,

$$C^{\mathrm{d}} = \left(\frac{\varepsilon_0 \varepsilon v_+^2 z_+^2 cF^2}{2RT}\right)^{1/2}\frac{\left|\exp(-z_+ y^{\mathrm{d}}) - \exp(-z_- y^{\mathrm{d}})\right|}{\left[v_+ \exp(-z_+ y^{\mathrm{d}}) + v_- \exp(-z_- y^{\mathrm{d}}) - v_+ - v_-\right]^{1/2}} \tag{4-55}$$

or in the following way,

$$C^{\mathrm{d}} = \varepsilon_0 \varepsilon \kappa \left[\frac{v_+ z_+}{2(z_+ - z_-)} \right]^{1/2} \frac{\left| \exp(-z_+ y^{\mathrm{d}}) - \exp(-z_- y^{\mathrm{d}}) \right|}{\left[v_+ \exp(-z_+ y^{\mathrm{d}}) + v_- \exp(-z_- y^{\mathrm{d}}) - v_+ - v_- \right]^{1/2}} \tag{4-56}$$

with the reciprocal Debye length κ given, for the present case, by,

$$\kappa^2 = \frac{cF^2}{\varepsilon_0 \varepsilon RT} \left(v_+ z_+^2 + v_- z_-^2 \right) \tag{4-57}$$

Thus, in the plot of C^{d} *vs.* y^{d}, the capacitance minimum generally does not coincide with the zero point of the diffuse layer potential for asymmetrical electrolytes, but it is shifted in the direction where the multivalent ion is the co-ion.

The potential distribution

Similar to that for electrolyte mixtures, no general analytical formula can be given for $y(x)$ for asymmetrical electrolytes. However, in special cases where the electrolyte is or may be regarded as symmetrical, the PB equation can be solved analytically on the basis of the Gouy-Chapman theory.

For a symmetrical electrolyte, for which $v_+ = v_- = 1$ and $z_+ = -z_- = z$, Equation 4-49 reduces to,

$$\frac{\mathrm{d}^2(zy)}{\mathrm{d}x^2} = \kappa^2 \sinh(zy) \tag{4-58}$$

with the reciprocal Debye length κ given, for the present case, by,

$$\kappa^2 = \frac{2F^2 cz^2}{\varepsilon_0 \varepsilon RT} \tag{4-59}$$

where we have used $c_+ = c_- = c$.

Integration of Equation 4-58, following the same procedure from Equation 4-20 to Equation 4-25, yields,

$$\frac{\mathrm{d}y}{\mathrm{d}x} = -\frac{2\kappa}{z} \sinh\left(\frac{zy}{2} \right) \tag{4-60}$$

This equation can be integrated once again, using the boundary condition that $y = y^{\mathrm{d}}$ at $x = 0$, to give the analytical solution of the potential distribution in a diffuse double layer,

$$\tanh\left(\frac{zy}{4} \right) = \tanh\left(\frac{zy^{\mathrm{d}}}{4} \right) \exp(-\kappa x) \tag{4-61}$$

Introducing γ to stand for the hyperbolic tangent,

$$\gamma = \tanh\left(\frac{zy}{4} \right) \tag{4-62}$$

we may abbreviate Equation 4-61 as,

$$\gamma = \gamma^{\mathrm{d}} \exp(-\kappa x) \tag{4-63}$$

In the limit case of low potentials (i.e. when the Debye-Hückel approximation holds), the hyperbolic tangent may be replaced by the first, linear, term of its series expansion, to give Equations 4-39 and 4-40. This has been approved to be a good approximation for $zy \leq 2$ ($\psi \leq 50$ mV for $z = 1$, $\psi \leq 25$ mv for $z = 2$, etc).

Another situation of interest in which Equation 4-61 simplifies considerably is the case of large values of x at which the potential has fallen to a small value regardless of its initial value. Under these conditions, the hyperbolic tangent on the l.h.s. of Equation 4-61 may be replaced by the first term of its series expansion. This gives,

$$zy = 4\gamma^{\mathrm{d}} \exp(-\kappa x) \qquad \text{for large values of } x \tag{4-64}$$

For very large values of y^{d}, γ^{d} goes to unity, and then the above equation becomes,

$$zy = 4 \exp(-\kappa x) \qquad \text{for large values of } y^{\mathrm{d}} \text{ and } x \tag{4-65}$$

This expression shows clearly that, in the case of large diffuse potentials, the potential in the outer portion of the diffuse double layer would be independent of the inner potential.

On the other hand, with Equation 4-60 at hand, we may characterize the diffuse double layer in a relatively simple way for the case where only one symmetrical electrolyte is involved.

The electric field strength

From Equation 4-60, the electric field strength in a diffuse double layer is immediately found as,

$$E = \sqrt{\frac{8cRT}{\varepsilon_0 \varepsilon}} \sinh\left(\frac{zF\psi}{2RT}\right) \tag{4-66}$$

In the limit of low potentials, when the Debye-Hückel approximation holds, it reduces then to Equation 4-41.

The diffuse charge

With the help of Equation 4-29, the diffuse charge can be found directly from Equation 4-66 for $x \to 0$, to give,

$$\sigma^{\mathrm{d}} = -\sqrt{8\varepsilon_0 \varepsilon cRT} \sinh\left(\frac{zy^{\mathrm{d}}}{2}\right) = -\varepsilon_0 \varepsilon \kappa \psi^{\mathrm{d}} \frac{\sinh(zy^{\mathrm{d}}/2)}{zy^{\mathrm{d}}/2} \tag{4-67}$$

The inverse of this equation can be written as,

$$y^{\mathrm{d}} = \frac{2}{z} \ln\left[-\varphi\sigma^{\mathrm{d}} + \sqrt{(\varphi\sigma^{\mathrm{d}})^2 + 1}\right] \tag{4-68}$$

with

$$\varphi = (8\varepsilon_0 \varepsilon cRT)^{-1/2} \tag{4-69}$$

The differential capacitance

The differential capacitance of a diffuse double layer can, for the present case, be found from differentiation of Equation 4-67 with respect to ψ^{d}, and it can conveniently be written as,

$$C^{\mathrm{d}} = \varepsilon_0 \varepsilon \kappa \cosh\left(\frac{zy^{\mathrm{d}}}{2}\right) = \varepsilon_0 \varepsilon \kappa \left[1 + \frac{(zy^{\mathrm{d}})^2}{8} + \mathrm{O}(zy^{\mathrm{d}})^4\right] \tag{4-70}$$

Thus, just like the charge, C^{d} increases proportionally to $c^{1/2}$ because of screening.

Moreover, the above expression shows that, in the plot of C^{d} *vs.* y^{d}, the capacitance is an even function and symmetrical with respect to the point of zero charge. The capacitance is, however, finite at that point the charge is zero and equal to,

$$\mathrm{C}^{\mathrm{d}} = \varepsilon_0 \varepsilon \kappa \qquad (\sigma^{\mathrm{d}} = 0) \tag{4-71}$$

which is nothing else than the formula for a flat condenser with plate distance κ^{-1}.

The Gibbs energy

The Gibbs energy per unit area can now also be computed for a purely diffuse double layer by combination of Equations 4-9 and 4-67; this gives,

$$\Delta G_{\mathrm{a}}^{\sigma} = -\frac{8cRT}{\kappa}\left[\cosh\left(\frac{zy^{\mathrm{d}}}{2}\right) - 1\right] \tag{4-72}$$

It may be rewritten, with Equations 4-70 and 4-71 at hand, as,

$$\Delta G_{\mathrm{a}}{}^{\sigma} = -\frac{8cRT}{\varepsilon_0\varepsilon\kappa^2}\left[C^{\mathrm{d}} - C^{\mathrm{d}}(y^{\mathrm{d}} = 0)\right] \tag{4-73}$$

It is seen that this quantity is a measure of the screening. However, it should be noted that capacitances are purely electrostatic quantities whereas the Gibbs energy has a non-electrostatic root.

The ionic components of charge

In the Gouy-Chapman model, we can write the ionic components simply as,

$$\sigma_{+}^{\mathrm{d}} = zF\int_0^{\infty}\left[c_{+}(x) - c_{+}(\infty)\right]\mathrm{d}x = zFc\int_0^{\infty}\left[\exp(\text{-}zy)\text{ -}1\right]\mathrm{d}x \tag{4-74}$$

and

$$\sigma_{-}^{\mathrm{d}} = -zF\int_0^{\infty}\left[c_{-}(x) - c_{-}(\infty)\right]\mathrm{d}x = -zFc\int_0^{\infty}\left[\exp(zy)\text{ -}1\right]\mathrm{d}x \tag{4-75}$$

Integrations can be carried out with the help of Equation 4-60, i.e.,

$$\int_0^{\infty}\left[\exp(\text{-}zy)\text{ -}1\right]\mathrm{d}x = \int_{y^{\mathrm{d}}}^{0}\frac{\left[\exp(\text{-}zy)\text{ -}1\right]\mathrm{d}y}{\mathrm{d}y/\mathrm{d}x} = \int_{y^{\mathrm{d}}}^{0}\frac{\left[\exp(\text{-}zy)\text{ -}1\right]\mathrm{d}y}{-(\kappa/z)\left[\exp(zy/2)\text{ - }\exp(\text{-}zy/2)\right]} \tag{4-76}$$

Subsequently, it gives,

$$\int_0^{\infty}\left[\exp(\text{-}zy)\text{ -}1\right]\mathrm{d}x = \frac{z}{\kappa}\int_{y^{\mathrm{d}}}^{0}\exp(\text{-}zy/2)\mathrm{d}y \tag{4-77}$$

In this way, one obtains,

$$\sigma_{+}^{\mathrm{d}} = \frac{2czF}{\kappa}\left[\exp(\text{-}zy^{\mathrm{d}}/2)\text{ - }1\right] \tag{4-78}$$

Similarly,

$$\sigma_{-}^{\mathrm{d}} = \frac{2czF}{\kappa}\left[1\text{ - }\exp(zy^{\mathrm{d}}/2)\right] \tag{4-79}$$

These two components of charge satisfy the requirement of Equation 4-3, and for low potentials reduce to,

$$\sigma_{+}^{\mathrm{d}} = \sigma_{-}^{\mathrm{d}} = -\mathrm{c}\mathrm{z}^2 Fy^{\mathrm{d}}/\kappa \tag{4-80}$$

On the other hand, with increasingly positive y^{d}, the excess charge attributed by anions increases exponentially, whereas the excess charge attributed by cations asymptotically approaches the limit,

$$\lim_{\mathrm{y}^{\mathrm{d}}\to\infty}\sigma_{+}^{\mathrm{d}} = -2czF/\kappa \tag{4-81}$$

This expression shows that in the limit of maximum expulsion effectively two Debye lengths of the double layer are devoid of co-ions.

4.3 The Stern model

It is not difficult to point to a number of imperfections in the Poisson-Boltzmann theory. These mainly include the following /19/:

1. The finite sizes of the ions are neglected.
2. Non-Coulombic interaction between counter- and co-ions and surface (specific adsorption) is disregarded.
3. The permittivity of the medium is assumed to be constant.
4. Incomplete dissociation of the electrolyte is ignored.
5. The average potential and the potential of the mean force are assumed to be identical.
6. The solvent is considered to be primitive.
7. Polarization of the solvent by the charged surface is not taken into account.
8. The surface charge is assumed to be homogeneous and smeared-out.
9. Surfaces are considered flat on a molecular scale.
10. Image forces between ions and the surface are neglected.

Considering this long list of iniquities, it is not surprising that conditions are readily found where the Poisson-Boltzmann model breaks down. A typical illustration is that at high surface potential ($y^0 >> 1$) the double layer charge and capacitance on mercury and silver iodide remain far below that predicted. On most surfaces and in many electrolytes specific adsorption is observed (different σ^0 for different ions of the same valency at given pAg, pH, etc). The extent of it and the sequence depend on the natures of the surface and electrolyte. On the other hand, perfect applicability of Poisson-Boltzmann equations is observed in other experiments. For instance, interaction forces at not too short distance between two charged surfaces, as measured in the surface force apparatus and the effect of the electrolyte concentration on the thickness of the liquid films and on the negative adsorption are all well described. Hence, it is appropriate to delineate the domain of applicability of the Poisson-Boltzmann theory and to consider appropriate corrections. This leads to development of the Stern model that has over the decades since its inception rendered excellent services, especially in dealing with experimental systems.

In the Stern model, the solution side of the double layer is, following the older ideas of Helmholtz, subdivided generally into two parts: an inner part, or Stern layer where all complications regarding finite ion size, specific adsorption, discrete charges, surface heterogeneity, etc, reside and an outer part, Gouy or diffuse layer where ions can move in any directions. The diffuse layer is by definition ideal, i.e. it obeys the Poisson-Boltzmann statistics. The borderline between the Stern layer and the diffuse layer, though somewhat artificial, is usually called the outer Helmholtz plane (oHp), whereas the plane where all specifically adsorbed ions, if considered, reside is called the inner Helmholtz plane (iHp).

The Stern layer may, however, have different structures, depending on the detail and the complexity involved. Correspondingly, we may classify the Stern models into several categories, as being discussed below.

4.3.1 The zeroth-order Stern model

In this simple model, as illustrated schematically in Figure 4-1, only the effect of finite ion size is considered by ignoring the existence of the inner Helmholtz plane.

Therefore, the Stern layer is charge-free and it acts as a molecular condenser in which the potential decreases linearly with the distance from the surface, i.e.

$$\Delta^2 \psi = 0 \qquad (4\text{-}82)$$

Thus, the potential distribution in the Stern layer of thickness d is given, for flat surfaces, by,

$$\psi = \psi^0 + (\psi^d - \psi^0)x/d \qquad \text{at} \qquad 0 \le x \le d \qquad (4\text{-}83)$$

where the potential of the diffuse part ψ^d is lower than when the entire double layer were diffuse because then ψ^d would have been equal to ψ^0.

In the diffuse layer, the charge distribution remains by definition ideal, meaning that all the relevant equations of the Poisson-Boltzmann theory remain valid after replacing x by x-d. Hence, in the following, we pay our attention mainly on the Stern layer, discussing about its physical properties.

The capacitance

Similar to Equation 4-34 for the diffuse layer, the differential capacitance to the Stern layer is given by,

$$C^{\mathrm{s}} = \frac{\mathrm{d}\sigma^0}{\mathrm{d}(\psi^0 - \psi^{\mathrm{d}})} \tag{4-84}$$

and correspondingly the integral capacitance reads,

$$K^{\mathrm{s}} = \frac{\sigma^0}{\psi^0 - \psi^{\mathrm{d}}} \tag{4-85}$$

where the superscript s has been added to both C and K as a reminder that it applies only for the Stern layer.

Since the charge balance Equation 4-32 still holds for electrical double layers for this simple case, we can write,

$$C^{\mathrm{s}} = -\frac{\mathrm{d}\sigma^{\mathrm{d}}}{\mathrm{d}(\psi^0 - \psi^{\mathrm{d}})} \qquad \text{and} \qquad K^{\mathrm{s}} = -\frac{\sigma^{\mathrm{d}}}{\psi^0 - \psi^{\mathrm{d}}} \tag{4-86}$$

Thus, at given σ^0 and ψ^0, combination of Equations 4-31, 4-34 and 4-86 gives,

$$\frac{1}{C} = \frac{1}{C^{\mathrm{s}}} + \frac{1}{C^{\mathrm{d}}} \qquad \text{and} \qquad \frac{1}{K} = \frac{1}{K^{\mathrm{s}}} + \frac{1}{K^{\mathrm{d}}} \tag{4-87}$$

That is, the total double layer capacitance consists of two capacitances in series. The smaller of the two gives the main contribution to the overall capacitance.

In general, however, both C^s and K^s depend on σ^0 and ψ^0 (because the relative dielectric permittivity in the Stern layer, ε^s, depends on the electric field) but only indirectly on the electrolyte concentration (because it affects σ^0 at given ψ^0).

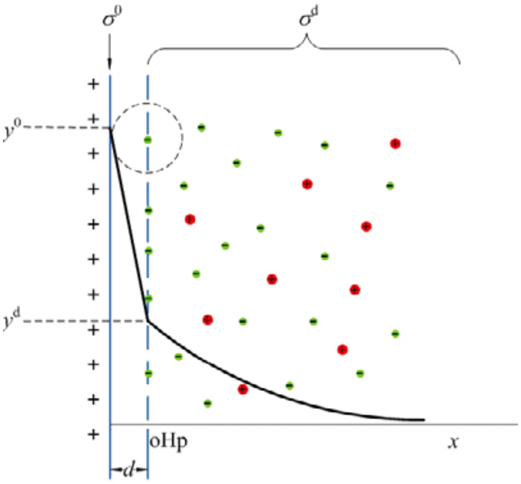

Figure 4-1. *Identification of the various planes and potentials associated with an electric double layer in the zeroth-order Stern layer model.*

Using Gauss' law at a given σ^0, we have,

$$\left.\frac{\mathrm{d}\psi}{\mathrm{d}x}\right|_{x=0} = -\frac{\sigma^0}{\varepsilon_0 \varepsilon^{\mathrm{s}}} \tag{4-88}$$

from which the integral capacitance can be found as,

$$K^{\mathrm{s}} = \frac{\varepsilon_0 \varepsilon^{\mathrm{s}}}{d} \tag{4-89}$$

Hence, when the quotient is independent of σ^0 or ψ^0, the differential capacitance is also a constant and can, with the help of interconversion between the two capacitances, also be written as,

$$C^{\mathrm{s}} = \frac{\varepsilon_0 \varepsilon^{\mathrm{s}}}{d} \tag{4-90}$$

The Gibbs energy

The capacitances C^{s} and K^{s} not only dictate the difference between ψ^{d} and ψ^0, but also are useful in quantifying the Gibbs energy for Gouy-Stern layers.

Qualitatively, the zeroth-order Stern model differs from the purely diffuse model in that the screening is poorer. Higher potentials are required to obtain a certain surface charge. Quantitatively, we have in principle Equation 4-9 for the purely diffuse case for the relaxed double layers, which in the zeroth-order Stern model can be modified to account for the fact that ψ can now maximally become ψ^{d}. To that end, it is more expedient and transparent to decompose the electrical contributions to the Gibbs energy into two components by considering the existence of the outer Helmholtz plane (oHp). Thus, we may write,

$$\Delta G_{\mathrm{a}}^{\sigma} = -\int_0^{\sigma^{\mathrm{d}}} \psi^{\mathrm{d}'} \mathrm{d}\sigma^{\mathrm{d}'} + \int_0^{\sigma^0} (\psi^{0'} - \psi^{\mathrm{d}'}) \mathrm{d}\sigma^{0'} - \psi^0 \sigma^0 \tag{4-91}$$

The first two integrals, representing the purely electric contributions, can be understood by visualizing the charging process to occur in two steps. First a charge $\sigma^0 = -\sigma^{\mathrm{d}}$ is brought to the outer Helmholtz plane; the (positive) electrical work is represented by the first integral. Second, this charge, to become the surface charge, is transported from there to the surface, for which the second integral, also positive, is the electrical work involved. The non-electric contributions, represented by the third term, is nothing else than that for purely diffuse models.

Mathematically, however, combination of these three terms immediately yields,

$$\Delta G_{\mathrm{a}}^{\sigma} = -\int_0^{\psi^0} \sigma^{0'} \mathrm{d}\psi^{0'} \tag{4-92}$$

This result is identical to Equation 4-9, for purely diffuse double layers. In words, the Gibbs energy for a double layer with a charge-free inner layer is the same as that for a purely diffuse layer, the quantitative difference being that at given ψ^0, σ^0 is lower. No additional terms are needed for the charge-free layer because all ions are diffuse and, hence, do not contribute.

On the other hand, we may replace the first integral by,

$$-\int_0^{\sigma^{\mathrm{d}}} \psi^{\mathrm{d}'} \mathrm{d}\sigma^{\mathrm{d}'} = -\sigma^{\mathrm{d}} \psi^{\mathrm{d}} + \int_0^{\psi^{\mathrm{d}}} \sigma^{\mathrm{d}'} \mathrm{d}\psi^{\mathrm{d}'} \tag{4-93}$$

and the second integral by, with the help of Equation 4-86 for a constant capacitance of the inner layer (implying $K^{\mathrm{s}} = C^{\mathrm{s}}$),

$$\int_0^{\sigma^0} (\psi^{0'} - \psi^{\mathrm{d}'}) \mathrm{d}\sigma^{0'} = \frac{(\sigma^0)^2}{2C^{\mathrm{s}}} \tag{4-94}$$

and then making use of the charge balance Equation 4-32, we arrive at,

$$\Delta G_{\mathrm{a}}^{\sigma} = -\frac{(\sigma^0)^2}{2C^{\mathrm{s}}} + \int_0^{\psi^{\mathrm{d}}} \sigma^{\mathrm{d'}} \mathrm{d}\psi^{\mathrm{d'}} \tag{4-95}$$

This is a useful formula because the integral on the r.h.s. is the equation for a purely diffuse layer ($\sigma^{0'} = -\sigma^{\mathrm{d'}}$ in this case), whereas the first term modifies it for the charge-free layer. Moreover, this formula shows that the purely diffuse limit is obtained for $C^{\mathrm{s}} \to \infty$.

Thus, using Equation 4-72 for a symmetrical electrolyte, the above equation becomes,

$$\Delta G_{\mathrm{a}}^{\sigma} = -\frac{(\sigma^0)^2}{2C^{\mathrm{s}}} - \frac{8cRT}{\kappa}\left[\cosh\left(\frac{zy^{\mathrm{d}}}{2}\right) - 1\right] \tag{4-96}$$

4.3.2 The triple layer model

In more general cases, specific adsorption should also be taken into account in addition to finite ion size. Then, the inner Helmholtz plane (iHp) where specifically adsorbed ions reside splits the Stern layer into two parts, as sketched in Figure 4-2; an inner part, or inner Helmholtz layer of thickness β, is located between the charged surface and the inner Helmholtz plane, and an outer part, or outer Helmholtz layer of thickness γ, located between the inner and the outer Helmholtz planes.

In both layers, the potentials decrease linearly with the distance from the surface, i.e. both of them act as molecular condensers in which Equation 4-82 also hold.

For flat surfaces, the potential distribution in the Stern layer can thus be explicitly written as,

$$\psi = \psi^0 + (\psi^{\mathrm{s}} - \psi^0)\, x/\beta \qquad \text{for} \qquad 0 \le x \le \beta \tag{4-97}$$

and

$$\psi = \psi^{\mathrm{s}} + (\psi^{\mathrm{d}} - \psi^{\mathrm{s}})\frac{x-\beta}{d-\beta} \qquad \text{for} \qquad \beta \le x \le d \tag{4-98}$$

where ψ^{s} denotes the potential at the inner Helmholtz plane.

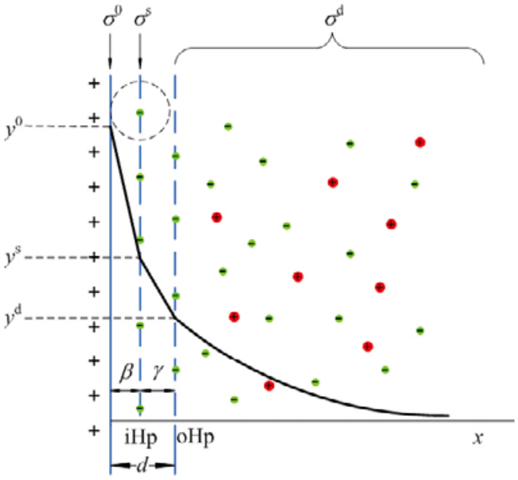

Figure 4-2. *Identification of the various planes and potentials associated with an electric double layer in the triple layer model.*

The capacitance

In this triple layer model, three charges and three capacitances can be distinguished. For the two inner layers differential capacitances are defined as,

$$C_1^{\mathrm{s}} = \frac{\mathrm{d}\sigma^0}{\mathrm{d}(\psi^0 - \psi^{\mathrm{s}})} \tag{4-99}$$

$$C_2^{\mathrm{s}} = \frac{\mathrm{d}(\sigma^0 + \sigma^{\mathrm{s}})}{\mathrm{d}(\psi^{\mathrm{s}} - \psi^{\mathrm{d}})} \tag{4-100}$$

where σ^{s} stands for the specifically adsorbed charge.

The corresponding integral capacitances then read,

$$K_1^{\mathrm{s}} = \frac{\sigma^0}{\psi^0 - \psi^{\mathrm{s}}} \tag{4-101}$$

$$K_2^{\mathrm{s}} = \frac{\sigma^0 + \sigma^{\mathrm{s}}}{\psi^{\mathrm{s}} - \psi^{\mathrm{d}}} \tag{4-102}$$

In this case, the charge balance equation becomes,

$$\sigma^0 + \sigma^{\mathrm{s}} + \sigma^{\mathrm{d}} = 0 \tag{4-103}$$

Hence, we can write,

$$C_2^{\mathrm{s}} = -\frac{\mathrm{d}\sigma^{\mathrm{d}}}{\mathrm{d}(\psi^{\mathrm{s}} - \psi^{\mathrm{d}})} \qquad \text{and} \qquad K_2^{\mathrm{s}} = -\frac{\sigma^{\mathrm{d}}}{\psi^{\mathrm{s}} - \psi^{\mathrm{d}}} \tag{4-104}$$

It follows immediately that, at given σ^0 and ψ^0,

$$\psi^0 - \psi^{\mathrm{d}} = \frac{\sigma^0}{K_1^{\mathrm{s}}} - \frac{\sigma^{\mathrm{d}}}{K_2^{\mathrm{s}}} \tag{4-105}$$

and

$$\frac{1}{C} = \frac{1}{C_1^{\mathrm{s}}} - \left(\frac{1}{C_2^{\mathrm{s}}} + \frac{1}{C^{\mathrm{d}}}\right)\frac{\mathrm{d}\sigma^{\mathrm{d}}}{\mathrm{d}\sigma^0} \tag{4-106}$$

These results show that, in this case, C^{s} or K^{s} cannot be split into two components in series, and therefore, the total double layer capacitance cannot be simply represented by three capacitances in series.

At a given σ^0, however, the counterpart of Equation 4-89 can be given by,

$$K_1^{\mathrm{s}} = \frac{\varepsilon_0\varepsilon_1^{\mathrm{s}}}{\beta} \qquad \text{and} \qquad K_2^{\mathrm{s}} = \frac{\varepsilon_0\varepsilon_2^{\mathrm{s}}}{\gamma} \tag{4-107}$$

and, if both capacitances are constant (invariant with σ^0 or ψ^0), we would have,

$$C_1^{\mathrm{s}} = \frac{\varepsilon_0\varepsilon_1^{\mathrm{s}}}{\beta} \qquad \text{and} \qquad C_2^{\mathrm{s}} = \frac{\varepsilon_0\varepsilon_2^{\mathrm{s}}}{\gamma} \tag{4-108}$$

Note that in general $C_1^{\mathrm{s}} \neq C_2^{\mathrm{s}}$ and $K_1^{\mathrm{s}} \neq K_2^{\mathrm{s}}$, although it is not easy to say by how much they differ because interpretation of capacitances in terms of macroscopic parameters like ε and thickness is by no means physically realistic on the scale of one or two molecular diameters.

The Gibbs energy

To compute the Gibbs energy for Gouy-Stern layers, we may simply extend the charging process leading to Equation 4-91. First, a charge $(\sigma^0 + \sigma^{\mathrm{s}}) = -\sigma^{\mathrm{d}}$ is brought to the outer Helmholtz plane, then it is moved to the inner Helmholtz plane, and finally part of this charge, σ^0, is transported from there to the surface. In the triple layer model, however, the non-electric contributions to the Gibbs energy should be discriminated between those for the charge-determining and specifically adsorbing ions. For charge-determining ions, the expression is exactly the same one as Equation 4-8, i.e.

$$\Delta G^{\sigma}_{\mathrm{a,\,cd}}\,(\mathrm{nonel.}) = \psi^{0}\sigma^{0} \tag{4-109}$$

while for specifically adsorbed ions, we have,

$$\Delta G^{\sigma}_{\mathrm{a,\,sa}}\,(\mathrm{nonel.}) = -\psi^{\mathrm{s}}\sigma^{\mathrm{s}} \tag{4-110}$$

because specific adsorption at the inner Helmholtz plane also proceeds until balanced by the opposing electrical contribution.

Hence, generally,

$$\Delta G^{\sigma}_{\mathrm{a}} = -\int_{0}^{\sigma^{\mathrm{d}}}\psi^{\mathrm{d}'}\mathrm{d}\sigma^{\mathrm{d}'} - \int_{0}^{\sigma^{\mathrm{d}}}(\psi^{s'} - \psi^{\mathrm{d}'})\mathrm{d}\sigma^{\mathrm{d}'} + \int_{0}^{\sigma^{0}}(\psi^{0'} - \psi^{s'})\mathrm{d}\sigma^{0'} - \psi^{0}\sigma^{0} - \psi^{\mathrm{s}}\sigma^{\mathrm{s}} \tag{4-111}$$

By virtue of charge balance, Equation 4-103, it is readily verified that this expression is consistent with Equation 4-11.

Now, introducing Equations 4-99 and 4-100 for the differential capacitances of the inner and outer Helmholtz layers and assuming both to be constant (differential and integral capacitances would then be identical), the above equation yields,

$$\Delta G^{\sigma}_{\mathrm{a}} = -\frac{(\sigma^{0})^{2}}{2C^{\mathrm{s}}_{1}} - \frac{(\sigma^{\mathrm{d}})^{2}}{2C^{\mathrm{s}}_{2}} + \int_{0}^{\psi^{\mathrm{d}}}\sigma^{\mathrm{d}'}\mathrm{d}\psi^{\mathrm{d}'} \tag{4-112}$$

This is obviously an extension of Equation 4-95.

Hence, using Equation 4-72 for a symmetrical electrolyte, the above equation becomes,

$$\Delta G^{\sigma}_{\mathrm{a}} = -\frac{(\sigma^{0})^{2}}{2C^{\mathrm{s}}_{1}} - \frac{(\sigma^{\mathrm{d}})^{2}}{2C^{\mathrm{s}}_{2}} - \frac{8cRT}{\kappa}\left[\cosh\left(\frac{zy^{\mathrm{d}}}{2}\right) - 1\right] \tag{4-113}$$

This equation shows that the Gibbs energy has a diffuse contribution plus two addition terms, weighted by the two reciprocal capacitances. The purely diffuse case is retrieved only when these capacitances are infinitely high.

4.3.3 Variant form of the triple layer model

A great difficulty of applying the triple layer model is to assess ψ^{s}, which is required to formulate an adsorption isotherm for counterions. This quantity is quite esoteric. In some cases ψ^{s} is identified with ψ^{0}, but this is a very poor approximation. Somewhat better, simpler models, somewhere between the zeroth and first order have been proposed. Two of them are:

(1) Ignore the break in $\mathrm{d}\psi/\mathrm{d}x$ at the inner Helmholtz plane. Then ψ^{s} is simply related to ψ^{0} and ψ^{d} as,

$$\psi^{\mathrm{s}} = \frac{\gamma\psi^{0} + \beta\psi^{\mathrm{d}}}{\gamma + \beta} \tag{4-114}$$

(2) Assume that specific adsorption takes place at the outer Helmholtz plane. This means that the inner Helmholtz plane no longer exists and therefore ψ^{s} is identified with ψ^{d}. In this case, Equation 4-106 reduces to,

$$\frac{1}{C} = \frac{1}{C^{\mathrm{s}}} - \frac{1}{C^{\mathrm{d}}}\frac{\mathrm{d}\sigma^{\mathrm{d}}}{\mathrm{d}\sigma^{0}} \tag{4-115}$$

and correspondingly Equation 4-112 becomes,

$$\Delta G^{\sigma}_{\mathrm{a}} = -\frac{(\sigma^{0})^{2}}{2C^{\mathrm{s}}} + \int_{0}^{\psi^{\mathrm{d}}}\sigma^{\mathrm{d}'}\mathrm{d}\psi^{\mathrm{d}'} \tag{4-116}$$

This result is identical to Equation 4-95 for the zeroth-order approximation. It implies that the Gibbs energy for a double layer with a charge-free inner layer, but with specific adsorption at the outer Helmholtz plane, is the same as that without specific adsorption. The quantitative difference is that, at given ψ^0, σ^0 is lower in the latter case.

Other assumptions, such as setting the relative dielectric constant of the outer Helmholtz layer equals to that of the bulk value, do not lead to simpler formulations. Neither do that regarding the position of the outer Helmholtz plane, this is the reason why it is usually assumed in the triple layer model that the charge density at the outer Helmholtz plane is zero (i.e. no ion resides on this plane) without any consideration. However, if the outer Helmholtz plane is taken to be located at the centre of the first row of counterions, we may, by setting up a force balance to the outer Helmholtz plane, arrive at the following expression /20/,

$$\frac{\sigma^{\mathrm{oHp}}}{\sigma^0+\sigma^{\mathrm{s}}}=-\frac{n^2-1}{\varepsilon_2^s} \qquad (4\text{-}117)$$

where σ^{oHp} denotes the charge density at the outer Helmholtz plane, and n is the optical refractive index of the bulk solution (for water, it is about 1.33 at 300K).

Using Gauss' law for this specific case, the effective surface charge density ($\sigma^0 + \sigma^{\mathrm{s}}$) can be expressed as a function of the electric field, i.e.

$$\sigma^0+\sigma^{\mathrm{s}}=\varepsilon_0\varepsilon_2^{\mathrm{s}}E|_{x=\beta} \qquad (4\text{-}118)$$

Also, the relative dielectric constant of the double layers depends strongly on the electric field. For water we can write /20/,

$$\varepsilon=n^2+\frac{7\rho_{\mathrm{w}}p_{\mathrm{w}}^2(n^2+2)}{3\varepsilon_0\sqrt{73}E}L\left(\frac{\sqrt{73}Ep_{\mathrm{w}}^2(n^2+2)}{6k_{\mathrm{B}}T}\right) \qquad (4\text{-}119)$$

where ρ_{w} is water density, p_{w} is electric dipole of a single water molecule (2.02 Debye units) and the Langevin function is given by,

$$L(x)=\coth(x)-1/x \qquad (4\text{-}120)$$

Thus, combination of these equations could be used to evaluate the ratio on the l.h.s. of Equation 4-117 as a function of the effective surface charge density. The result shows that the charge density σ^{oHp} at the outer Helmholtz plane, if it is explicitly positioned, is negligible only in the case when ($\sigma^0 + \sigma^{\mathrm{s}}$) is smaller than 10 µC/cm².

4.3.4 Specific adsorption of ions

Specific adsorption of ions is, as stated previously, their adsorption by non-electrostatic forces. By this mechanism, ions can accumulate on a surface even against electrostatic repulsion. The non-electric Gibbs energy of adsorption generally depends on the nature of ions and the surface, hence the term "specific". In practice, sometimes situations are met where ions do not specifically adsorb on an uncharged surface, but do so once there are charges on the surface, such as alkali ions on iodide. Wherever appropriate, we shall call this type specific adsorption of the second kind.

Since the Stern theory pays much attention on specific adsorption, an approach has to be provided to determine the specifically adsorbed charge, σ^{s}, at each σ^0. In other words, to complete the triple layer model, one needs an adsorption isotherm equation.

Theoretically, this could be done straightforwardly on the basis of the isotherm equations available for uncharged molecules: simply an electrostatic contribution $z_{\mathrm{j}}F\psi^{\mathrm{s}}$ has to be added to the non-electrostatic Gibbs energy of adsorption. Multilayer specific adsorption of ions does not have to be considered, because ions beyond the Stern layer are (by definition) generically adsorbed.

As we mostly consider surface charges, residing on certain sites at the surface, localized adsorption is the most likely mechanism. Lateral interaction is, because of the long range of the electrostatic forces and the usually low degrees of occupancy, dominated by the electrostatic forces and in the mean field treatment accounted for by a $z_{\mathrm{j}}F\psi^{\mathrm{s}}$ term.

Under these conditions the specific or non-electrostatic adsorption Gibbs energy is only determined by the ion-surface interaction. Hence, an intrinsic binding constant can be introduced as /19/,

$$K_j = \exp(-\Delta_{ads}G_j/RT) \qquad (4\text{-}121)$$

where $\Delta_{ads}G_j$ denotes the specific adsorption Gibbs energy per mol of j species adsorbed.

At low coverages, it is often a good approximation to assume K_j to be constant. However, the total Gibbs energy of adsorption is not constant because the electrostatic part changes with σ^0. Note also that this equation requires K_j to be dimensionless. When K_j is not dimensionless and nevertheless this equation is still used, the implication is that $\Delta_{ads}G_j$ is referred to an (arbitrary) reference, determined by the concentration units /19/.

With thee K_j expression at hand, we may now formulate adsorption isotherm equations. To that end, assumptions have to be made about the kinds of ions that bind, and on the planes where they adsorb. Stern himself considered the specific adsorption of cations and anions, both at the outer Helmholtz plane. More likely are situations where only one ionic type adsorbs at the inner Helmholtz plane. For that case, the Langmuir Equation is readily extended by adding the electrostatic contribution, $z_jF\psi^s$, to the non-electrostatic adsorption Gibbs energy. Thus, for a charged adsorbate, we obtain,

$$\frac{\theta_j}{1-\theta_j} = x_jK_j\exp(-z_jF\psi^s/RT) \qquad (4\text{-}122)$$

with the fraction of surface coverage, θ_j, given by,

$$\theta_j = N_j/N_0 \qquad (4\text{-}123)$$

where x_j is the mole fraction of ions of type j in the bulk solution, N_j and N_0 are the number of specifically adsorbed ions and the number of sites per unit area of the surface, respectively (the N_0 adsorption sites for specifically adsorbing ions are not necessarily identical to those for surface ions. The specifically adsorbed charge can be smaller or larger than the surface charge).

Making θ_j explicit and introducing,

$$\sigma^s = z_jeN_j \qquad (4\text{-}124)$$

the above equation gives, with the help of Equation 4-17,

$$\sigma^s = \frac{z_jeN_0K_j\exp(-z_jy^s)x_j}{1+K_j\exp(-z_jy^s)x_j} \qquad (4\text{-}125)$$

A variant of this equation applies to the case where, say positive, charges on the surface act as the sites where specific adsorption of anions may take place, i.e. when the specific adsorption is of the second kind. Then, ion pairs are formed and held together by both electrostatic and non-electrostatic interactions. For that case, the surface charge is,

$$\sigma^0 = -z_jeN_0 \qquad (4\text{-}126)$$

and the specifically adsorbed charge can be given by, with the help of Equation 4-123,

$$\sigma^s = -\theta_j\sigma^0 \qquad (4\text{-}127)$$

Hence, using the charge balance Equation 4-103, the diffuse charge reads,

$$\sigma^d = (\theta_j-1)\,\sigma^0 \qquad (4\text{-}128)$$

and Equation 4-125 becomes,

$$\sigma^s = -\frac{\sigma^0K_j\exp(-z_jy^s)x_j}{1+K_j\exp(-z_jy^s)x_j} \qquad (4\text{-}129)$$

In summary, it is not difficult to formulate Stern adsorption isotherm equations. The main problem is to determine y^s, for which assumptions have to be made. First, there is the assumption of the mean field, and then the localization of the inner Helmholtz plane is at issue. The quality of these models is not easily assessed, but ultimately comparison with the experiments is decisive.

5 Overlapping double layers

When discussing about electrostatic interactions resulting from overlapping of double layers, the term homo-interaction is used for the interaction between particles that have identical values of the potential and/or charge, irrespective of the nature of the particles and solvents, whereas the term hetero-interaction refers to when particles have different potentials and/or charges.

5.1 Homo-interaction

We start by considering the simplest situation of two identical particles, each carrying identical electrical double layers, embedded in a solution of fixed concentrations (i.e. having fixed chemical potentials) of an electrolyte, containing charge-determining ions and an indifferent electrolyte. The particles are assumed not to settle down, but to move randomly by Brownian motion. When they meet upon a chance encounter, repulsion is felt. We may ask, why? The answer is not as obvious as may appear at first sight. The most direct, but oversimplified reply, "because they are charged, and equal charges repel each other", is immediately parried by the equally oversimplified counter-statement that the double layers do not interact at all electrostatically because, as a whole, they are un-charged. In the nineteen thirties this issue occupied the minds of some colloid scientists; there are even papers concluding that the electric interaction between identical particles is repulsive at a certain distances but attractive at others. Had the diffuse double layers been spatially fixed, then one could imagine a repulsion at long distance (because of overlap of the extreme parts of these double layers, carrying charges of the same sign) and attraction at shorter distance (because the surface charge of the one particle starts to attract the countercharge of the other). However, diffuse double layers are not static. They can, and will, regulate their structures upon overlap, leading to a change in entropy which also contributes to the Gibbs energy of interaction /21/.

Thus, for relaxed double layers, the surface potential y^0 is expected to be fixed upon interaction, because the concentration of charge-determining ions remains constant in the system, so that the Nernst equilibrium would be retained. When y^0 is fixed (at its value for separation $s \rightarrow \infty$), the surface charge σ^0 should decrease upon overlap; in Verwey-Overbeek language, by desorption of charge-determining ions. The reason for this is that the proximity of the second surface with the same charge makes it unattractive for such ions to be on the surface. Eventually, in the limit $s \rightarrow 0$, $\sigma^0 \rightarrow 0$. With this in mind, it becomes evident that at least part of the disjoining pressure Π_{el} is of a chemical nature.

Double layers in isolation form spontaneously by adsorption and desorption of charge-determining ions. Hence, the adsorption of such ions is inhibited when a second particle approaches, meaning that work has to be done against their chemical affinity. Stated otherwise, the particles repel each other. Usually, this mechanism is called, interaction at constant potential, or surface charge regulation, since such a type of interaction requires adjustment of the surface charge.

The alternative, interaction at constant charge, applies to systems with fixed surface charges, such as polystyrene sulphate lattices or the plates of clay minerals. In this case, y^0 shoots up upon overlap of polarized double layers and the corresponding contribution to the Gibbs energy of interaction is of a purely electrical nature (because no adsorption and desorption takes place). Consequently, we may also call this process, surface potential regulation, since such a type of interaction requires adjustment of the surface potential.

Not only because of the neglect of the Stern layer, but also on dynamic grounds, can something be stated against these mechanisms. For many systems with initially relaxed double layers, surface ions simply do not have the time to desorb during a Brownian encounter. Then, there are two options: (1) the system behaves as a system of constant charge or, (2), the surface charge proper will not decrease, but it is made ineffective by adsorption of counterions. The latter mechanism requires a Stern layer over which the countercharge is regulated. Intermediate cases can also be imagined, depending on the nature and magnitudes of the ion fluxes and their yields on the time scale of a Brownian collision.

5.1.1 Interaction at constant potential

This type of interaction rarely occurs in practice because there is no reason for y^d, the potential of the diffuse part of the double layer, to remain fixed upon interaction. Only in the absence of a Stern layer may y^d be replaced by y^0, the surface potential, which may remain constant as far as it is determined by Nernst's law. However, as we shall show later on, double layers that are purely diffuse exist only at very low surface potentials and low electrolyte concentration. In the more realistic situation of overlap between two Gouy-Stern double layers, regulation across the Stern layer never leads to constancy of y^d.

Nevertheless, we shall start the description for the simple case of fixed y^d because it contains a number of relevant principles and steps that recur in other cases. Physically speaking it means that for the moment we ignore Stern layers and dynamic issues.

Interaction in a symmetrical electrolyte

Consider now two identical parallel flat particles, with identical diffuse double layers, embedded in one symmetrical (z-z) electrolyte at fixed p and T. Upon approach, $y(x)$ between the two surfaces is, as sketched in Figure 5-1, increased above the value it would have had for one single double layer. As the potentials at the surface ($y^d = y^0$ in this case) are assumed to remain fixed, the slopes ($\mathrm{d}y/\mathrm{d}x$) near the two surfaces decrease. Because of Gauss' law we have for the left double layer,

$$\left(\frac{\mathrm{d}y}{\mathrm{d}x}\right)_{x\to 0} = -\frac{\sigma^0 F}{\varepsilon_0 \varepsilon RT} \tag{5-1}$$

quantifying the reduction of the surface charge in terms of the slope, i.e. in terms of the electric field adjacent to the surface and

$$\left(\frac{\mathrm{d}y}{\mathrm{d}x}\right)_{x\to h} = -\frac{\sigma^0 F}{\varepsilon_0 \varepsilon RT} \tag{5-2}$$

for the right double layer.

For homo-interaction, the minimum potential y^m is half way between the two plates. At this minimum, the field strength is zero, meaning that the total charges, including those on the surfaces, between $x = 0$ and $x = x^m$, and between $x = x^m$ and $x = h$ are zero. However, the potential at the minimum is not zero, meaning that an out force is needed to maintain it at the increased value.

The midway potential

To find out the potential distribution, we must integrate the Poisson-Boltzmann Equation 4-58 for the range between $x = 0$ and $x = h$. For easy reference, we write this equation once again,

$$\frac{\mathrm{d}^2(zy)}{\mathrm{d}x^2} = \kappa^2 \sinh(zy) \tag{5-3}$$

In the previous chapter, we demonstrated how it can be integrated. The result is,

$$\left(\frac{\mathrm{d}y}{\mathrm{d}x}\right)^2 = \frac{2\kappa^2}{z^2}\left[\cosh(zy) + C\right] \tag{5-4}$$

The integration constant C can be found from the boundary condition that at the midway between the two plates $\mathrm{d}y/\mathrm{d}x = 0$ and $y = y^m$; this gives,

$$C = -\cosh(zy^m) \tag{5-5}$$

Hence, we have,

$$\frac{\mathrm{d}y}{\mathrm{d}x} = \mp\frac{\kappa}{z}\sqrt{2\left[\cosh(zy) - \cosh(zy^m)\right]} \tag{5-6}$$

For $0 \leq x \leq x^{\mathrm{m}}$, we need the minus sign because y is a decreasing function of x. For the right half, $x^{\mathrm{m}} \leq x \leq h$, the plus sign is need.

To find the midway potential, y^{m}, an integration of Equation 5-6 over one half of the x-range is needed. This gives /22/,

$$-\frac{\kappa h}{2} = \int_{y^{\mathrm{d}}}^{y^{\mathrm{m}}} \frac{z\mathrm{d}y}{\sqrt{2\left[\cosh(zy) - \cosh(zy^{\mathrm{m}})\right]}} \tag{5-7}$$

The result can be written as,

$$\kappa h = 2\exp\left(-\frac{zy^{\mathrm{m}}}{2}\right) F\left\{\exp\left(-\frac{zy^{\mathrm{m}}}{2}\right), \frac{\pi}{2}\right\} - F_{\mathrm{E}}\left\{\exp\left(-\frac{zy^{\mathrm{m}}}{2}\right), \sin^{-1}\left[\exp\left(-\frac{zy^{\mathrm{d}} - zy^{\mathrm{m}}}{2}\right)\right]\right\} \tag{5-8}$$

with the elliptic integral of the first kind given by,

$$F_{\mathrm{E}}(\phi, \vartheta) = \int_0^{\vartheta} \frac{d\chi}{\sqrt{1 - \phi^2 \sin^2\chi}} \tag{5-9}$$

Thus, an exact numerical solution is available for the midway potential. However, it is too complicated to be used in practice and approximate solutions should be sought for some limiting cases.

To that end, we may consider the case where the overlap of double layers is so weak that y^{m} is determined by linear superposition of the two constituting potentials. In this LSA approximation, deformation of double layers upon overlap is ignored. Hence, it applies only to very weak overlap, $\kappa h/2 >> 1$, irrespective the value of y^{d}, which might be high. When this approximation holds, there is no difference between the electrostatic interaction at constant potential and at constant charge. It depends on h, and hence, on the type of measurement whether the LSA is satisfactory.

Recall from Equation 4-61 that for a single double layer the potential decay is given by,

$$\tanh\left(\frac{zy}{4}\right) = \tanh\left(\frac{zy^{\mathrm{d}}}{4}\right)\exp(-\kappa x) \tag{5-10}$$

If applied to the midway situation $y \rightarrow y^{\mathrm{m}}$, $x \rightarrow h/2$, and as a large κh corresponds with a low y^{m} the hyperbolic tangent on the l.h.s. may be replaced by the first term of its series expansion. Thus, in the LSA, we have,

$$zy^{\mathrm{m}} = 8\tanh\left(\frac{zy^{\mathrm{d}}}{4}\right)\exp\left(-\frac{\kappa h}{2}\right) \tag{5-11}$$

This expression shows that y^{m} increases linearly with y^{d} if the latter potential is low, but becomes independent of y^{d} when y^{d} is very high.

On the other hand, if the overlap of double layers is very strong, the Poisson-Boltzmann Equation 5-3 can appropriately be linearized with respect to the derivation of y from y^{d}. In this Ohshima approximation /23/, the potential distribution near the plate surface can be written as,

$$zy = zy^{\mathrm{d}} - \tanh(zy^{\mathrm{d}})\left\{1 - \frac{\cosh\left[\sqrt{\cosh(zy^{\mathrm{d}})}(\kappa h/2 - \kappa x)\right]}{\cosh\left[\sqrt{\cosh(zy^{\mathrm{d}})}(\kappa h/2)\right]}\right\} \tag{5-12}$$

This expression can be used to evaluate y^{m} only for the case of strong overlap, $\kappa h/2 << 1$. On setting $x = h/2$ in Equation 5-12, we obtain the following relationship between y^{m} and y^{d},

$$zy^{\mathrm{m}} = zy^{\mathrm{d}} - \tanh(zy^{\mathrm{d}})\left\{1 - \frac{1}{\cosh\left[\sqrt{\cosh(zy^{\mathrm{d}})}(\kappa h/2)\right]}\right\} \tag{5-13}$$

For small κh, it reduces to,

$$zy^{\mathrm{m}} = zy^{\mathrm{d}} - \frac{1}{8}\sinh(zy^{\mathrm{d}})(\kappa h)^2 \tag{5-14}$$

The diffuse charge

For the diffuse charge, combination of Equations 5-1 and 4-32 gives,

$$\sigma^{\mathrm{d}} = \frac{\varepsilon_0 \varepsilon RT}{F}\left(\frac{\mathrm{d}y}{\mathrm{d}x}\right)_{x\to 0} \tag{5-15}$$

The potential slope at the r.h.s. is obtained directly from Equation 5-6. Thus, we find,

$$\sigma^{\mathrm{d}} = -\left(\mathrm{sign} y^{\mathrm{d}}\right)\frac{2czF}{\kappa}\sqrt{2\left[\cosh(zy^{\mathrm{d}}) - \cosh(zy^{\mathrm{m}})\right]} \tag{5-16}$$

Consequently, with the help of Equation 4-59, it can be rewritten as,

$$\sigma^{\mathrm{d}} = -\left(\mathrm{sign} y^{\mathrm{d}}\right)\sqrt{4\varepsilon_0 \varepsilon cRT\left[\cosh(zy^{\mathrm{d}}) - \cosh(zy^{\mathrm{m}})\right]} \tag{5-17}$$

For $y^{\mathrm{m}} = 0$, this equation reduces to Equation 4-67, giving the surface charge density of one isolated double layer, $\sigma^{\mathrm{d}}(h = \infty)$.

Therefore, in the LSA, we can simply substitute Equation 5-11 into the above equation to obtain σ^{d}. In the Ohshima approximation, however, it is better to work directly on Equation 5-15, by substitution of Equation 5-12. The result is,

$$\sigma^{\mathrm{d}} = -\frac{2czF}{\kappa}\tanh(zy^{\mathrm{d}})\sqrt{\cosh(zy^{\mathrm{d}})}\tanh\left[\sqrt{\cosh(zy^{\mathrm{d}})}(\kappa h/2)\right] \tag{5-18}$$

For small κh, it reduces to,

$$\sigma^{\mathrm{d}} = -czF \sinh(zy^{\mathrm{d}})h \tag{5-19}$$

Thus, Equation 5-18 has the correct limiting form as $\kappa h \to 0$, but it does not reduce to Equation 4-67 in the limit $\kappa h \to \infty$.

The Gibbs energy of interaction

To compute the electrical contribution to the Gibbs energy of interaction, $G_{\mathrm{a,el}}$, we may consider two relaxed double layers, originally far apart ($h \to \infty$), embedded in a solution of constant composition, i.e. with p, T and all chemical potentials fixed, and adsorption equilibrium is assumed to prevail. When the distance between the particles is reduced from ∞ to h, the only changes that occur thermodynamically are those in the two surface excess Gibbs energies. Hence,

$$G_{\mathrm{a,el}} = 2\left[\Delta G_{\mathrm{a}}^{\sigma}(h) - \Delta G_{\mathrm{a}}^{\sigma}(\infty)\right] \tag{5-20}$$

where the Δ's may be dropped because both terms refer to the same reference state of no adsorption.

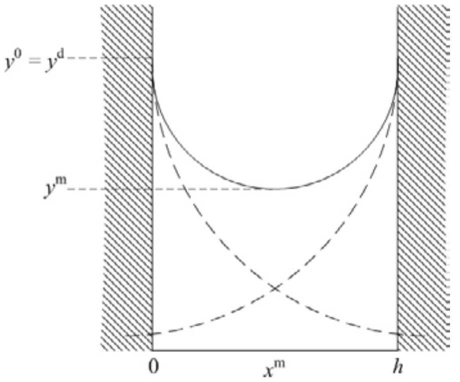

Figure 5-1. *Schematic representation of the dimensionless potential between two identical parallel flat diffuse double layers. The dashed curves are the profiles for the two double layers far apart. The spatial variable x is counted from the l.h.s. plate.*

The Gibbs energy of one isolated diffuse double layer is already available, and generally it is given by Equation 4-9. If only one symmetrical electrolyte is involved, Equation 4-72 is the solution. For easy reference, we may rewrite the latter equation as,

$$\Delta G_{\mathrm{a}}^{\sigma}(\infty) = -\frac{8cRT}{\kappa}\left[\cosh\left(\frac{zy^{\mathrm{d}}}{2}\right) - 1\right] \tag{5-21}$$

The Gibbs energy of the overlapped diffuse double layer can also be found by a charging process along the line used for that of the isolated one. The only difference is that the integration does not take place from 0 to y^{d}, but from y^{m} to y^{d}. Thus, similar to Equation 4-9, we can write,

$$\Delta G_{\mathrm{a}}^{\sigma}(h) = \frac{RT}{F}\int_{y^{\mathrm{m}}}^{y^{\mathrm{d}}} \sigma^{\mathrm{d'}}\mathrm{d}y^{\mathrm{d'}} \tag{5-22}$$

As y^{m} is known from Equation 5-8, the integral can be solved. However, this requires a laborious mathematical procedure /22/, for which we give no details here.

Substitution of Equations 5-21 and 5-22 gives immediately $G_{\mathrm{a,el}}$. The result is,

$$G_{\mathrm{a,el}} = -2cRT\int_{0}^{h/2}\left[\cosh(zy) - 1\right]\mathrm{d}x + \frac{\varepsilon_0\varepsilon(RT)^2}{2F^2}\int_{0}^{h/2}\left(\frac{\mathrm{d}y}{\mathrm{d}x}\right)^2\mathrm{d}x \tag{5-23}$$

which can be converted into an integration over the potential,

$$G_{\mathrm{a,el}} = -\frac{2cRT}{\kappa}\left\{\frac{\kappa h}{4}\left(3e^{zy^{\mathrm{m}}} - 2 + e^{-zy^{\mathrm{m}}}\right) + 2\sqrt{2\left[\cosh(zy^{\mathrm{d}}) - \cosh(zy^{\mathrm{m}})\right]} + \right.$$
$$\left. + \int_{y^{\mathrm{m}}}^{y^{\mathrm{d}}} \frac{e^{-zy} - e^{zy^{\mathrm{m}}}}{\sqrt{2\left[\cosh(zy) - \cosh(zy^{\mathrm{m}})\right]}}\mathrm{d}y\right\} \tag{5-24}$$

As with Equation 5-7, this expression can be converted to elliptic functions, for which tables are available. Also, an approximate solution of $G_{\mathrm{a,el}}$ can be found for cases where the LSA is satisfactory. Then, substitution of Equation 5-11 into the above equation gives /22/,

$$G_{\mathrm{a,el}} = \frac{64cRT}{\kappa}\tanh^2\left(\frac{zy^{\mathrm{d}}}{4}\right)\exp(-\kappa h) \tag{5-25}$$

As the derivation of this equation is easier via the disjoining pressure than via Equation 5-24, we postpone this until the following subsection.

Equation 5-25 has, in fact, a fair validity range, as can be judged from comparison with the numerical solutions. It quantifies the independence of y^{d} at large y^{d} and the proportionality with $(y^{\mathrm{d}})^2$ if y^{d} is low. Moreover, it predicts an overall linearity of $\ln G_{\mathrm{a,el}}$ with κh. For low κh, however, Equation 5-25 overestimates $G_{\mathrm{a,el}}$ at low y^{d}, but under-estimates it at high y^{d}.

On the other hand, Equation 5-25 shows the dual effect of the electrolyte concentration. For $h \rightarrow 0$, $G_{\mathrm{a,el}}$ increases proportionally to $c^{1/2}$, i.e. proportionally to κ. However, higher κ implies stronger screening and hence $G_{\mathrm{a,el}}$ decreases rapidly with h.

The influence of the valency z is complicated: increase of z increases $G_{\mathrm{a,el}}$ at very short distance, but the decay is steeper. Perhaps the dominant effect is that at given potential y^0 multivalent counterions tend to lower y^{d} more than do monovalent ions. This is a feature that acts beyond the purely diffuse double layer.

Also, an approximate solution of $G_{\mathrm{a,el}}$ is available for cases of strong overlap, where the plate separation is small and hence the Ohshima approximation holds, and it is given by /23/,

$$G_{\mathrm{a,el}} = \frac{8cRT}{\kappa}\left\{\frac{2}{\kappa h}\ln\left[\frac{1 + \exp(-\kappa h)}{1 + \exp\left(-\kappa h\sqrt{\cosh(zy^{\mathrm{d}})}\right)}\right] + 2\cosh\left(\frac{zy^{\mathrm{d}}}{2}\right) - \sqrt{\cosh(zy^{\mathrm{d}}) - 1}\right\} \tag{5-26}$$

The disjoining pressure

There are two ways to obtain the disjoining pressure Π_{el}. The first is by differentiation of the Gibbs energy of interaction $G_{\mathrm{a,el}}$ with respect to the distance, as in Equation 1-1. In this way, Equation 5-24 or 5-25 and 5-26 can be used to obtain the exact solution or good approximations, respectively. The second approach is by identifying the force that has to be required to keep the plates at a certain distance. The basic idea is that overlap leads to an increase of the counterion concentration between the two plates, and hence to an osmotic pressure. This pressure depends on h, and at given h it also depends on the position x between the plates. In addition to this osmotic pressure there is also a pressure resulting from the electrostatic field known as the Maxwell stress, which also depends on x at given h. The sum of these two pressures must be independent of x, otherwise the system would be mechanically unstable, i.e., this sum is only a function of h.

Consider again the two identical parallel flat plates, a distance h apart. What is behind the plates does not matter. The intervening liquid must be in contact with an infinitely large reservoir of fixed composition, which can adsorb any electrolyte expelled from between the plates if h is reduced, and which also acts as a buffer for expelled electrolyte to keep the chemical potentials constant. In this scheme, no volume work and no work to change the chemical potentials are involved, and hence, Gibbs and Helmholtz energies are identical.

Now we bring the plates from infinite distance to a state where the double layers overlap. To keep the two plates at distance h in mechanical equilibrium upon an infinitesimal displacement, the change in the hydrostatic pressure dp plus the change in the electrical pressure, which can be written as $\rho \mathrm{d}\psi$, must be zero. In formula, we have,

$$\mathrm{d}p + \rho \mathrm{d}\psi = 0 \qquad (5\text{-}27)$$

Thus, substituting the Poisson's Equation 4-15 for ρ, we find,

$$\frac{\mathrm{d}p}{\mathrm{d}x} - \frac{\varepsilon_0 \varepsilon}{2} \frac{\mathrm{d}}{\mathrm{d}} \left(\frac{\mathrm{d}\psi}{\mathrm{d}x} \right)^2 = 0 \qquad (5\text{-}28)$$

It gives immediately, upon integration,

$$p - \frac{\varepsilon_0 \varepsilon}{2} \left(\frac{\mathrm{d}\psi}{\mathrm{d}x} \right)^2 = \text{const.} \quad \text{(independent of position)} \qquad (5\text{-}29)$$

This equation states clearly that the sum of the hydrostatic pressure and the Maxwell stress is independent of position x. Subtraction of the external pressure p_∞ (where the Maxwell stress is of course zero) gives Π_{el}, i.e.,

$$\Pi_{\mathrm{el}} = (p - p_\infty) - \frac{\varepsilon_0 \varepsilon}{2} \left(\frac{\mathrm{d}\psi}{\mathrm{d}x} \right)^2 \qquad \text{(independent of position)} \qquad (5\text{-}30)$$

The first term on the r.h.s. is the osmotic pressure p_{os}. which results from an increase of the counterion concentration. According to Boltzmann's law, as in Equation 4-12, for the symmetrical electrolyte under consideration, the excess concentration of counterions is $c(\mathrm{e}^{zy}\text{-}1)$ and that of co-ions $c(\mathrm{e}^{-zy}\text{-}1)$. The total excess concentration at any position x between the two plates is then given by $2c[\cosh(zy)\text{-}1]$, and hence, the ensuing osmotic pressure can simply be written as,

$$p_{\mathrm{os}} = p - p_\infty = 2cRT[\cosh(zy) - 1] \qquad (5\text{-}31)$$

Substitution of this expression into Equation 5-30 yields,

$$\Pi_{\mathrm{el}} = 2cRT[\cosh(zy) - 1] - \frac{\varepsilon_0 \varepsilon}{2} \left(\frac{\mathrm{d}\psi}{\mathrm{d}x} \right)^2 \qquad (5\text{-}32)$$

or, by Equation 4-17,

$$\Pi_{\mathrm{el}} = 2cRT[\cosh(zy) - 1] - \frac{\varepsilon_0 \varepsilon (RT)^2}{2F^2} \left(\frac{\mathrm{d}y}{\mathrm{d}x} \right)^2 \qquad (5\text{-}33)$$

Not surprisingly, this equation can also be obtained by differentiation of Equation 5-23 with respect to the distance h, as in Equation 1-1.

In addition, it should be noted that Equation 5-33 applies actually to any point between the plates. Thus, it is only necessary to know the potential and the potential gradient at some point between the plates in order to calculate the disjoining pressure. If we choose the plate surface to work with, Π_{el} can be written as, with the help of Equation 5-15,

$$\Pi_{\mathrm{el}} = 2cRT\left[\cosh(zy^{\mathrm{d}}) - 1\right] - \frac{(\sigma^{\mathrm{d}})^2}{2\varepsilon_0\varepsilon} \tag{5-34}$$

However, due to the symmetry of the system under consideration, it is wise to choose the mid-point between the plates, where the Maxwell stress becomes zero and therefore Π_{el} becomes equal to the osmotic pressure p_{os}. Thus, at the mid-point, Equation 5-33 gives,

$$\Pi_{\mathrm{el}} = 2cRT\left[\cosh(zy^{\mathrm{m}}) - 1\right] = 4cRT\sinh^2\left(\frac{zy^{\mathrm{m}}}{2}\right) \tag{5-35}$$

This equation can also be obtained directly from Equation 5-27, by which we can write,

$$\Pi_{\mathrm{el}} = \int_{\infty}^{h} \mathrm{d}p = -\int_{0}^{\psi_{\mathrm{m}}} \rho\,\mathrm{d}\psi \tag{5-36}$$

Because for a symmetrical electrolyte, we know from Equations 4-12 and 4-14 that,

$$\rho = -2czF\sinh(zy) \tag{5-37}$$

integration of Equation 5-36 would give Equation 5-35 immediately.

Equation 5-35 is deceptively simple, but requires a model to find the midway potential, y^{m}. In addition, it shows that the h-dependence of Π_{el} stems from the h-dependence of y^{m}.

Also, Equation 5-35 can be simplified very much for the case of low midway potentials (when the LSA is satisfactory). In that case, the hyperbolic cosine in Equation 5-35 can be replaced by the first two terms of its series expansion. This leads, in the LSA, to,

$$\Pi_{\mathrm{el}} = cRT(zy^{\mathrm{m}})^2 \tag{5-38}$$

Thus, substitution of Equation 5-11 for y^{m} gives,

$$\Pi_{\mathrm{el}} = 64cRT\tanh^2\left(\frac{zy^{\mathrm{d}}}{4}\right)\exp(-\kappa h) \tag{5-39}$$

Upon integration with respect to h, this leads to Equation 5-25 for the Gibbs energy of interaction. So, at least for this approximate case the equivalence is proved between the two methods for describing the repulsion. For the validity of Equation 5-39, similar things can be said, as given below Equation 5-25.

For the case where the overlap of double layers is very strong, $\kappa h/2 \ll 1$, with large zy^{m}, simplification of Equation 5-35 cannot be made in the same way as in the LSA. Then, we should apply the Ohshima approximation to Equation 5-35 directly, by substitution of Equation 5-13 or 5-14. If the latter equation was used for y^{m}, we have,

$$\Pi_{\mathrm{el}} = 2cRT\cosh\left[zy^{\mathrm{d}} - \frac{1}{8}\sinh(zy^{\mathrm{d}})(\kappa h)^2\right] - 2cRT \tag{5-40}$$

Alternatively, combination Equations 5-34 and 5-18 can be used to evaluate Π_{el}.

Interaction in the Debye-Hückel approximation

Generally, no analytical solutions can be given for Π_{el} and $G_{\mathrm{a,el}}$ if the two parallel flat plates are embedded in an electrolyte mixture. However, in cases of low y everywhere (i.e. when the Debye-Hückel approximation holds with $zy^{\mathrm{d}} \leq 3.46$), it is very easy to arrive at analytical expressions.

The midway potential

The starting equation is, of course, the linearized PB equation. For easy reference, we write Equation 4-36 once again here,

$$\frac{\mathrm{d}^2 y}{\mathrm{d}x^2} = \kappa^2 y \tag{5-41}$$

The general solution of this equation is,

$$y = A\cosh(\kappa x) + B\sinh(\kappa x) \tag{5-42}$$

which can be verified by substitution.

The integration constants A and B can be found from the boundary conditions, as shown in Figure 5-1. From $x = 0$ and $y = y^\mathrm{d}$, we find,

$$A = y^\mathrm{d} \tag{5-43}$$

and from $x = h$ and $y = y^\mathrm{d}$, we find,

$$B = y^\mathrm{d}\frac{1-\cosh(\kappa h)}{\sinh(\kappa h)} \tag{5-44}$$

Hence, the potential distribution between the two plates is given by,

$$\frac{y}{y^\mathrm{d}} = \cosh(\kappa x) + \frac{1-\cosh(\kappa h)}{\sinh(\kappa h)}\sinh(\kappa x) \tag{5-45}$$

For the midway potential, we then have,

$$\frac{y^\mathrm{m}}{y^\mathrm{d}} = \cosh\left(\frac{\kappa h}{2}\right) + \frac{1-\cosh(\kappa h)}{\sinh(\kappa h)}\sinh\left(\frac{\kappa h}{2}\right) \tag{5-46}$$

which can be reworked, by using the relationships between hyperbolic functions, to give,

$$y^\mathrm{m} = y^\mathrm{d}\operatorname{sech}\left(\frac{\kappa h}{2}\right) \tag{5-47}$$

The diffuse charge

Multiplication of the two sides of Equation 5-41 by 2(dy/dx) leads to,

$$\left(\frac{\mathrm{d}y}{\mathrm{d}x}\right)^2 = \kappa^2 y^2 + C \tag{5-48}$$

where the integration constant C can be found from dy/dx = 0 at $y = y^\mathrm{m}$. Hence,

$$\frac{\mathrm{d}y}{\mathrm{d}x} = \mp\kappa\sqrt{y^2 - (y^\mathrm{m})^2} \tag{5-49}$$

the minus sign applies to the left of the minimum, the plus sign to the right.

With this slope at hand, the diffuse charge can be determined from Equation 5-15. The result is,

$$\sigma^\mathrm{d} = -\left(\operatorname{sign} y^\mathrm{d}\right)\frac{\varepsilon_0\varepsilon\kappa RT}{F}\sqrt{(y^\mathrm{d})^2 - (y^m)^2} \tag{5-50}$$

Substitution of Equation 5-47 gives,

$$\sigma^\mathrm{d} = -\frac{\varepsilon_0\varepsilon\kappa RT y^\mathrm{m}}{F}\sinh\left(\frac{\kappa h}{2}\right) \tag{5-51}$$

or

$$\sigma^{\mathrm{d}} = -\frac{\varepsilon_0 \varepsilon \kappa R T y^{\mathrm{d}}}{F} \tanh\left(\frac{\kappa h}{2}\right) \tag{5-52}$$

Thus, with the help of Equation 4-42 for the diffuse charge of one isolated double layer, we have,

$$\sigma^{\mathrm{d}} = \sigma_{\infty}^{\mathrm{d}} \tanh\left(\frac{\kappa h}{2}\right) \tag{5-53}$$

This suggests that the decrease of σ^{d} sets in only when $\kappa h/2 < 2$, to become substantial only below $\kappa h/2 \approx 1$, and all three parameters y^{d}, c and z influence the decrease.

The disjoining pressure

For an electrolyte mixture, we know from Equations 4-15 and 5-41 that in the Debye-Hückel approximation, the space charge density can simply be written as,

$$\rho = -\varepsilon_0 \varepsilon \kappa^2 \psi \tag{5-54}$$

Thus, working on Equation 5-36 gives,

$$\Pi_{\mathrm{el}} = \frac{\varepsilon_0 \varepsilon}{2} \left(\frac{\kappa R T y^{\mathrm{m}}}{F}\right)^2 \tag{5-55}$$

Immediately, substitution of Equation 5-47 leads to,

$$\Pi_{\mathrm{el}} = \frac{\varepsilon_0 \varepsilon}{2} \left(\frac{\kappa R T y^{\mathrm{d}}}{F}\right)^2 \operatorname{sech}^2\left(\frac{\kappa h}{2}\right) \tag{5-56}$$

Otherwise, by combination with Equation 5-51, we can express Π_{el} in terms of σ^{d},

$$\Pi_{\mathrm{el}} = \frac{(\sigma^{\mathrm{d}})^2}{2\varepsilon_0 \varepsilon} \operatorname{csch}^2\left(\frac{\kappa h}{2}\right) \tag{5-57}$$

At this stage, there can be no difference between interaction at constant potential and at constant charge, which only tells us what mechanism the final situation was reached. It should however be added that Equation 5-56 is preferable for the former case, whereas Equation 5-57 for the latter case. On the other hand, for very special cases where only one symmetrical electrolyte is considered in the Debye-Hückel approximation, Equation 5-56 can be rewritten as, by substitution of Equation 4-59 for κ,

$$\Pi_{\mathrm{el}} = cRT(zy^{\mathrm{d}})^2 \operatorname{sech}^2\left(\frac{\kappa h}{2}\right) \tag{5-58}$$

It can also be obtained directly from Equation 5-38 by substitution of Equation 5-47.

If, further, applying Equation 5-10 to the plate surface $y \to y^{\mathrm{d}}$, $x \to 0$ (because y is low everywhere), we get,

$$zy^{\mathrm{d}} \approx 4 \tanh\left(\frac{zy^{\mathrm{d}}}{4}\right) \tag{5-59}$$

which can be used to extend the potential range of Equation 5-58 without affecting the trends in the decay of Π_{el}.

Thus, replacing zy^{d} in Equation 5-58 by the r.h.s. of the above expression yields,

$$\Pi_{\mathrm{el}} = 16cRT \tanh^2\left(\frac{zy^{\mathrm{d}}}{4}\right) \operatorname{sech}^2\left(\frac{\kappa h}{2}\right) \tag{5-60}$$

This equation is generally valid provided the interaction is not very strong.

The Gibbs energy of interaction

Upon integration of Equation 5-56 with respect to h, we obtain the Gibbs energy of interaction, which can be written as,

$$G_{\mathrm{a,el}} = \varepsilon_0 \varepsilon \kappa \left(\frac{RTy^{\mathrm{d}}}{F} \right)^2 \left[1 - \tanh\left(\frac{\kappa h}{2} \right) \right] \tag{5-61}$$

Thus, for very special cases where only one symmetrical electrolyte is considered in the Debye-Hückel approximation, it becomes, by substitution of Equation 4-59 for κ or by integration of Equation 5-58 directly,

$$G_{\mathrm{a,el}} = \frac{2cRT(zy^{\mathrm{d}})^2}{\kappa} \left[1 - \tanh\left(\frac{\kappa h}{2} \right) \right] \tag{5-62}$$

which reads explicitly,

$$G_{\mathrm{a,el}} = \frac{4cRT(zy^{\mathrm{d}})^2}{\kappa} \frac{e^{-\kappa h}}{1 + e^{-\kappa h}} \tag{5-63}$$

This equation exhibits the usual exponential decay at large κh, but shows that for low κh the decay is less steep.

Likewise, the same procedure from Equation 5-58 to Equation 5-60 can be applied to improve the validity range of Equation 5-62. The result is,

$$G_{\mathrm{a,el}} = \frac{32cRT}{\kappa} \tanh^2\left(\frac{zy^{\mathrm{d}}}{4} \right) \left[1 - \tanh\left(\frac{\kappa h}{2} \right) \right] \tag{5-64}$$

5.1.2 Interaction at constant charge

We now focus on the case that upon interaction the diffuse charge σ^{d} remains fixed, as a result of which ψ^{d} has to increase. Physically, situations of constant charge will be met for parallel clay particles provided the surface charge and the electrolyte concentration are so low that Stern layer corrections are negligible.

Interaction in a symmetrical electrolyte

Consider again two parallel flat plates, a distance h apart, embedded in a symmetrical electrolyte at fixed p and T. In Figure 5-2, the distribution of charge from each plate is shown as if the other plate were absent. Now, an essential feature of the interaction of double layers at constant charge is that the total diffuse charge remains constant. As the plates approach each other this charge is compressed into a decreasing volume and so the charge density in the region between the plates increases, giving a repulsive force.

The midway potential

To find y^{m}, we should also start from the Poisson-Boltzmann Equation 5-3. However, for the present case, it is convenient to introduce a new dimensionless variable,

$$\eta = \frac{z\mathrm{d}y}{\kappa \mathrm{d}x} \tag{5-65}$$

Then, Equation 5-3 becomes,

$$\frac{\mathrm{d}\eta}{\mathrm{d}x} = \kappa \sinh(zy) \tag{5-66}$$

and the result of integration is given in Equation 5-6, which can now be rewritten as,

$$\eta^2 + \cosh(zy^{\mathrm{m}}) = 2\cosh(zy) \tag{5-67}$$

Immediately, we have,

$$[\eta^2 + 2\cosh(zy^{\mathrm{m}})]^2 = 4\,[1 + \sinh^2(zy)] \tag{5-68}$$

Hence, by using the relationships between hyperbolic functions, we obtain,

$$\left[\eta^2 + 4\cosh^2(zy^{\mathrm{m}}/2)\right]\left[\eta^2 + 4\sinh^2(zy^{\mathrm{m}}/2)\right] = 4\sinh^2(zy) \tag{5-69}$$

Following this, substitution of Equation 5-66 gives,

$$\left[\eta^2 + 4\cosh^2(zy^{\mathrm{m}}/2)\right]\left[\eta^2 + 4\sinh^2(zy^{\mathrm{m}}/2)\right] = 4\left(\frac{\mathrm{d}\eta}{\kappa\mathrm{d}x}\right)^2 \tag{5-70}$$

Thus, we have,

$$\frac{2\mathrm{d}\eta}{\kappa\mathrm{d}x} = \mathrm{sign}(zy^{m})\sqrt{\left[\eta^2 + 4\cosh^2(zy^{\mathrm{m}}/2)\right]\left[\eta^2 + 4\sinh^2(zy^{\mathrm{m}}/2)\right]} \tag{5-71}$$

and integration from $x = 0$ to $x = h/2$ can be performed,

$$\int_0^{h/2} \kappa\mathrm{d}x = \int_{\eta_0}^{0} \frac{2\mathrm{d}\eta}{\mathrm{sign}(zy^{m})\sqrt{\left[\eta^2 + 4\cosh^2(zy^{\mathrm{m}}/2)\right]\left[\eta^2 + 4\sinh^2(zy^{\mathrm{m}}/2)\right]}} \tag{5-72}$$

where η_0 is the value of η at $x = 0$, a scaled surface charge density, and it can be obtained from Equation 5-1 as,

$$\eta_0 = -\frac{zF\sigma^0}{\varepsilon_0\varepsilon\kappa RT} \tag{5-73}$$

The result is,

$$\kappa h = \int_0^{|\eta_0|} \frac{4\mathrm{d}\eta}{\sqrt{\left[\eta^2 + 4\cosh^2(zy^{\mathrm{m}}/2)\right]\left[\eta^2 + 4\sinh^2(zy^{\mathrm{m}}/2)\right]}} \tag{5-74}$$

This can be expressed in terms of elliptic integral as /24/,

$$\kappa h = 2\,\mathrm{sech}\left(\frac{zy^{\mathrm{m}}}{2}\right) F_{\mathrm{E}}\left\{\mathrm{sech}\left(\frac{zy^{\mathrm{m}}}{2}\right), \tan^{-1}\left[\frac{\eta_0}{2}\mathrm{csch}\left(\frac{zy^{\mathrm{m}}}{2}\right)\right]\right\} \tag{5-75}$$

where the elliptic integral of the first kind, F_{E}, has been defined in Equation 5-9.

Thus, an exact numerical solution is also available for the midway potential for the case of interaction at constant charge. However, it is too complicated to be used in practice and, as with the case of interaction at constant potential, approximate solutions should be sought for some limiting cases.

In this regard, as we discussed previously, there is no difference between the electrostatic interaction at constant potential and at constant charge in the LSA approximation. This implies that Equation 5-11 is also valid for the present case. However, it expresses y^{m} in terms of y^{d}, which does not remain constant but increases upon approach of the two plates with constant charge. As a result, it becomes inconvenient to use Equation 5-11, because then a relationship between y^{d} and σ^0 (or σ^{d}) has to be provided, which is not directly available for the case of weak overlap with large κh.

Hence, it is preferable in the LSA to express y^{m} in terms of σ^0, instead of y^{d}, for the present case. To that end, we notice that Equation 5-71 also holds for a single double layer, if we replace y^{m} by zero. This gives,

$$\frac{2\mathrm{d}\eta}{\kappa\mathrm{d}x} = -\eta\sqrt{\eta^2 + 4} \tag{5-76}$$

Thus, integration of this equation from $x = 0$ to x can be performed,

$$\int_0^{x} \kappa\mathrm{d}x = -\int_{\eta}^{\eta_0} \frac{2\mathrm{d}\eta}{\eta\sqrt{\eta^2 + 4}} \tag{5-77}$$

and the result is,

$$\kappa x = \ln\left(\frac{\eta_0}{\eta}\frac{2+\sqrt{\eta^2+4}}{2+\sqrt{\eta_0^2+4}}\right) \tag{5-78}$$

Since at large x the potential has fallen to a small value with $|y| << 1$, it follows from Equation 4-60 that,

$$\eta \approx -zy \tag{5-79}$$

We then have, from Equation 5-78, for the region $|y| << 1$,

$$zy = -\frac{4\eta_0}{2+\sqrt{\eta_0^2+4}}\exp(-\kappa x) \tag{5-80}$$

This can be considered the surface charge equivalent of Equation 4-64.

With Equation 5-80 at hand, we can easily apply the LSA approximation to the case where the overlap of double layers is very weak. Hence, in the LSA, the constant charge equivalent of Equation 5-11 is given by,

$$zy^{\mathrm{m}} = -\frac{8\eta_0}{2+\sqrt{\eta_0^2+4}}\exp\left(-\frac{\kappa h}{2}\right) \tag{5-81}$$

Likewise, for the present case, the potential distribution near the plate surface can also be obtained by applying the Ohshima approximation /25/. That is, we may also linearize the Poisson-Boltzmann Equation 5-3 with respect to the derivation of y from y^{d}. In this case, however, the boundary condition at the plate surface is not $y = y^{\mathrm{d}}$ any more, as for the case of interaction at constant potential, but given by Equation 5-73 for a fixed σ^0. The result is, then, significantly different from Equation 5-12 and it can be written as /25/,

$$zy = zy^{\mathrm{d}} - \tanh(zy^{\mathrm{d}})\left\{1-\eta^0\frac{\sqrt{\cosh(zy^{\mathrm{d}})}}{\sinh(zy^{\mathrm{d}})}\frac{\cosh\left[\sqrt{\cosh(zy^{\mathrm{d}})}(\kappa h/2-\kappa x)\right]}{\sinh\left[\sqrt{\cosh(zy^{\mathrm{d}})}(\kappa h/2)\right]}\right\} \tag{5-82}$$

Strictly speaking, this expression applies only for the region very near the surface. Thus, it can be used to evaluate y^{m} appropriately only for the case where the overlap of double layers is very strong such that $\kappa h/2 << 1$.

On setting $x = h/2$ in Equation 5-82, we obtain the following relationship between y^{m} and y^{d},

$$zy^{\mathrm{m}} = zy^{\mathrm{d}} - \tanh(zy^{\mathrm{d}})\left\{1-\frac{\sqrt{\cosh(zy^{\mathrm{d}})}}{\sinh(zy^{\mathrm{d}})}\frac{\eta^0}{\sinh\left[\sqrt{\cosh(zy^{\mathrm{d}})}(\kappa h/2)\right]}\right\} \tag{5-83}$$

For small κh, it reduces to,

$$zy^{\mathrm{m}} = zy^{\mathrm{d}} - \tanh(zy^{\mathrm{d}}) + \frac{\eta^0}{\cosh(zy^{\mathrm{d}})}\frac{2}{\kappa h} \tag{5-84}$$

It should, however, be noted that, for the present case, y^{d} adjusts itself upon interaction whereas σ^{d} is fixed. Thus, only when the relationship between y^{d} and σ^{d} is available can we use these equations in the Ohshima approximation.

The diffuse charge

Because there is no difference in the PB equation and the boundary condition half way the plates between interaction at constant potential and at constant charge, Equation 5-6 holds for both cases. Consequently, for the diffuse charge, Equation 5-16 or 5-17 is also valid for the present case. However, now, σ^{d} is fixed whereas y^{d} and y^{m} both depend on the distance h.

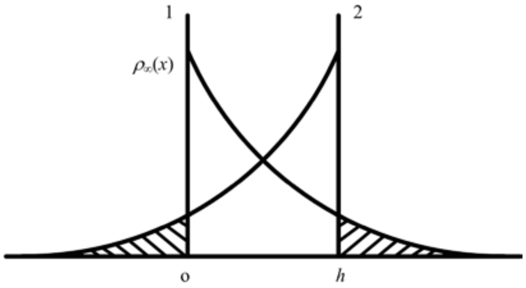

Figure 5-2. *Schematic representation of the variation of diffuse layer charge density with distance from charged plates. When the plates interact at constant charge an amount of charge indicated by the shaded areas has to be accommodated between the plates. The spatial variable x is counted from the l.h.s. plate.*

Thus, in the LSA, we can substitute Equation 5-11 into Equation 5-16 or 5-17 to determine implicitly how y^d or y^m changes with h. Otherwise, we can use the Ohshima approximation to obtain explicitly the relationship between y^d and σ^d (or σ^0).

On setting $x = 0$ in Equation 5-82, we obtain immediately /25/,

$$\sigma^{\mathrm{d}} = -\frac{2czF}{\kappa}\tanh(zy^{\mathrm{d}})\sqrt{\cosh(zy^{\mathrm{d}})}\tanh\left[\sqrt{\cosh(zy^{\mathrm{d}})}(\kappa h/2)\right] \tag{5-85}$$

This is exactly the same thing as Equation 5-18, and hence it holds for both cases. It should, however, be added that this equation does not give the correct limiting form as $\kappa h \rightarrow \infty$, i.e. Equation 4-67, which can now be written as,

$$\sigma^{\mathrm{d}} = -\frac{4czF}{\kappa}\sinh\left(\frac{zy_\infty^{\mathrm{d}}}{2}\right) \tag{5-86}$$

where the subscript ∞ has been added to y^d as a reminder that it applies only for an isolated double layer.

Nevertheless, as a good approximation for interaction at constant charge, combination of Equations 5-85 and 5-86 gives,

$$\tanh(zy^{\mathrm{d}}) = \frac{2\sinh(zy_\infty^{\mathrm{d}}/2)}{\sqrt{\cosh(zy^{\mathrm{d}})}\tanh\left[\sqrt{\cosh(zy^{\mathrm{d}})}(\kappa h/2)\right]} \tag{5-87}$$

For small κh, it reduces to,

$$\sinh(zy^{\mathrm{d}}) = \frac{2\sinh(zy_\infty^{\mathrm{d}}/2)}{\kappa h/2} \tag{5-88}$$

while for small zy^d, it can be approximated by,

$$\sinh(zy^{\mathrm{d}}) = \frac{2\sinh(zy_\infty^{\mathrm{d}}/2)}{\tanh(\kappa h/2)} \tag{5-89}$$

Because for small κh, the above equation tends to Equation 5-88, we deem that it gives a good approximation to Equation 5-87 even for large zy^d. Thus, in the case of strong overlap, we can use Equation 5-89 to estimate zy^d fairly well by /25/,

$$zy^{\mathrm{d}} = \sinh^{-1}\left[\frac{2\sinh(zy_\infty^{\mathrm{d}}/2)}{\tanh(\kappa h/2)}\right] \tag{5-90}$$

in which the diffuse potential of the isolated diffuse double layer can be determined from Equation 4-68 as a function of σ^d.

With this equation at hand, we can apply Equation 5-83 or 5-84 to give y^{m} at low κh in the Ohshima approximation.

The disjoining pressure

Following the concept of Π_{el}, we know that the disjoining pressure is, in fact, insensitive to the mode of charge regulation; it just represents a pressure at a given distance h and state of the surface. Thus, Equations 5-33, 5-34 and 5-35 all remain valid for Π_{el} for the case of interaction at constant charge.

Likewise, in the LSA, Equation 5-39 also works for the present case, but in practice it is seldom used because now no simple and direct relationship between y^{d} and σ^0 (or σ^{d}) is available for weak overlap. Hence, we should look for another route, to express Π_{el} directly in terms of σ^0 (or σ^{d}). To this end, we may substitute Equation 5-81 into 5-38 to give /24/,

$$\Pi_{\mathrm{el}} = 64cRT\left[\sqrt{1+\left(\frac{2}{\eta_0}\right)^2}-\frac{2}{\eta_0}\right]^2 \exp(-\kappa h) \qquad (5\text{-}91)$$

This equation may be considered the constant charge equivalent of Equation 5-39.

For the case where the overlap of double layers is very strong, however, Equation 5-40 is no longer valid because now the Ohshima approximation gives a different relationship between y^{m} and y^{d}, as in Equation 5-83. For the present case, we had better work on Equation 5-34 by substitution of Equation 5-90; this gives,

$$\Pi_{\mathrm{el}} = 2cRT\left[\sqrt{1+\frac{4\sinh^2(zy^{\mathrm{d}}_{\infty}/2)}{\tanh^2(\kappa h/2)}}-1\right]-\frac{(\sigma^{\mathrm{d}})^2}{2\varepsilon_0\varepsilon} \qquad (5\text{-}92)$$

Alternatively, in a more complicated way, combination of Equations 5-35, 5-83 and 5-90 can be used to evaluate Π_{el} at low κh.

The Gibbs energy of interaction

For interaction of diffuse double layers at constant potential, the surface charge adjusts itself upon approach of the particles, maintaining adsorption/desorption equilibrium at the surface. For interaction at constant charge, however, no adsorption or desorption takes place upon overlap, although the adsorption contribution, given by Equation 4-8, to the Gibbs energy of the diffuse double layer is of course retained. Thus, upon overlap the Gibbs energy of interaction, as in Equation 5-20, reduces to,

$$G^{(\sigma)}_{\mathrm{a,el}} = 2[\Delta G^{\sigma}_{\mathrm{a}}\,(\mathrm{el.})(h) - \Delta G^{\sigma}_{\mathrm{a}}\,(\mathrm{el.})(\infty)] \qquad (5\text{-}93)$$

where only the electrical contribution to the Gibbs energy of the double layer enters, and the superscript (σ) has been added to G as a reminder that it applies only at fixed charge.

Making $\Delta G^{\sigma}_{\mathrm{a}}$ (el.) explicit, by Equation 4-7, we obtain for purely diffuse double layers,

$$G^{(\sigma)}_{\mathrm{a,el}} = 2\left[-\int_0^{\sigma^{\mathrm{d}}}\psi^{\mathrm{d'}}\mathrm{d}\sigma^{\mathrm{d'}}+\int_0^{\sigma^{\mathrm{d}}}\psi^{\mathrm{d'}}_{\infty}\mathrm{d}\sigma^{\mathrm{d'}}\right] \qquad (5\text{-}94)$$

where in the second integral the subscript ∞ has been added to ψ as a reminder that it applies only for an isolated double layer.

If expressed in terms of y, we can write,

$$G^{(\sigma)}_{\mathrm{a,el}} = \frac{2RT}{F}\left[-\int_0^{\sigma^{\mathrm{d}}}y^{\mathrm{d'}}\mathrm{d}\sigma^{\mathrm{d'}}+\int_0^{\sigma^{\mathrm{d}}}y^{\mathrm{d'}}_{\infty}\mathrm{d}\sigma^{\mathrm{d'}}\right] \qquad (5\text{-}95)$$

This equation tells us that we must charge the diffuse double layer twice, first when the two surfaces are a distance h apart, then when they are isolated ($h \to \infty$). In both cases, the charging takes place from 0 to σ^{d}, i.e. to the diffuse charge for isolated particles. The two integrals differ because the relationship between y^{d} and σ^{d} is different for different overlap distances.

Working on this equation, integration by parts leads to,

$$G_{\mathrm{a,el}}^{(\sigma)} = \frac{2RT}{F}\left[-\sigma^{\mathrm{d}}(y^{\mathrm{d}} - y_{\infty}^{\mathrm{d}}) + \int_{0}^{y^{\mathrm{d}}}\sigma^{\mathrm{d'}}\mathrm{d}y^{\mathrm{d'}} - \int_{0}^{y^{\mathrm{d}}}\sigma_{\infty}^{\mathrm{d'}}\mathrm{d}y_{\infty}^{\mathrm{d'}} - \int_{y^{\mathrm{d}}}^{y_{\infty}^{\mathrm{d}}}\sigma_{\infty}^{\mathrm{d'}}\mathrm{d}y_{\infty}^{\mathrm{d'}}\right] \tag{5-96}$$

where we have split the integral for $h = \infty$ into two parts.

The sum of the first and second integral in the above equation is nothing else than the Gibbs energy of interaction for the constant potential case. Thus, we have,

$$G_{\mathrm{a,el}}^{(\sigma)} = G_{\mathrm{a,el}}^{(\psi)} - \frac{2RT}{F}\sigma^{\mathrm{d}}(y^{\mathrm{d}} - y_{\infty}^{\mathrm{d}}) - \frac{2RT}{F}\int_{y^{\mathrm{d}}}^{y_{\infty}^{\mathrm{d}}}\sigma_{\infty}^{\mathrm{d'}}\mathrm{d}y_{\infty}^{\mathrm{d'}} \tag{5-97}$$

In this equation, we may use Equation 5-86 for σ^{d}, and then the result is

$$G_{\mathrm{a,el}}^{(\sigma)} = G_{\mathrm{a,el}}^{(\psi)} + \frac{8cRT}{\kappa}\left[\left(zy^{\mathrm{d}} - zy_{\infty}^{\mathrm{d}}\right)\sinh\left(\frac{zy_{\infty}^{\mathrm{d}}}{2}\right) + 2\cosh\left(\frac{zy_{\infty}^{\mathrm{d}}}{2}\right) - 2\cosh\left(\frac{zy^{\mathrm{d}}}{2}\right)\right] \tag{5-98}$$

This equation always holds for interaction in a symmetrical electrolyte. Since the term in square brackets is always positive, we simply have,

$$G_{\mathrm{a,el}}^{(\sigma)} \geq G_{\mathrm{a,el}}^{(\psi)} \tag{5-99}$$

Therefore, interaction at constant charge is more repulsive than that at constant potential. The physical reason for this is that in the former situation the countercharge refuses to seep away when the force, exerted by the second double layer, is imposed.

The difference between the two Gibbs energies vanishes at such weak overlap that the LSA is satisfactory. Then, Equation 5-25 also works. However, the same reason as for Equation 5-39 makes it seldom used in practice. Hence, for the case of interaction at constant charge, we also prefer to express $G_{\mathrm{a,el}}$ directly in terms of σ^{0} (or σ^{d}). This could be done straightforwardly by integration of Equation 5-91 with respect to h, and then we have /24/,

$$G_{\mathrm{a,el}}^{(\sigma)} = \frac{64cRT}{\kappa}\left[\sqrt{1+\left(\frac{2}{\eta_0}\right)^2} - \frac{2}{\eta_0}\right]^2 \exp(-\kappa h) \tag{5-100}$$

This equation may be considered the constant charge equivalent of Equation 5-25.

For the case of strong overlap, however, similar equations as the above one cannot easily be obtained. In that case, the Ohshima approximation holds and thus we may substitute Equation 5-26, for the Gibbs energy of interaction at constant potential, into Equation 5-98 directly. This leads to /25/, for interaction at constant charge but at low κh,

$$\begin{aligned} G_{\mathrm{a,el}}^{(\sigma)} = \frac{8cRT}{\kappa}\Bigg\{&\frac{2}{\kappa h}\ln\left[\frac{1+\exp(-\kappa h)}{1+\exp\left(-\kappa h\sqrt{\cosh(zy^{\mathrm{d}})}\right)}\right] - \sqrt{\cosh(zy^{\mathrm{d}})} - 1 \\ &+ 2\cosh\left(\frac{zy_{\infty}^{\mathrm{d}}}{2}\right) + \left(zy^{\mathrm{d}} - zy_{\infty}^{\mathrm{d}}\right)\sinh\left(\frac{zy_{\infty}^{\mathrm{d}}}{2}\right)\Bigg\} \end{aligned} \tag{5-101}$$

This equation should be used in combination with Equations 5-90 and 4-68.

Interaction in the Debye-Hückel approximation

Based on the linear PB Equation 5-41, we have formulated analytical solutions of y^{d}, y^{m}, σ^{d}, Π_{el} and $G_{\mathrm{a,el}}$ for interaction of diffuse double layers at constant potential when y everywhere between the particles is fairly small in an electrolyte mixture. Assuming this Debye-Hückel approximation still holds for the constant charge case, Equations 5-51 and 5-52 would also be valid. However, now their variations are preferable because of a fixed σ^d. Thus, from Equation 5-52, we can write the surface potential as,

$$y^{\mathrm{d}} = -\frac{F\sigma^{\mathrm{d}}}{\varepsilon_0 \varepsilon \kappa RT}\coth\left(\frac{\kappa h}{2}\right) \tag{5-102}$$

or simply, by Equation 4-43,

$$y^{\mathrm{d}} = y_\infty^{\mathrm{d}}\coth\left(\frac{\kappa h}{2}\right) \tag{5-103}$$

Similarly, from Equation 5-51, we can write,

$$y^{\mathrm{m}} = -\frac{F\sigma^{\mathrm{d}}}{\varepsilon_0 \varepsilon \kappa RT}\operatorname{csch}\left(\frac{\kappa h}{2}\right) \tag{5-104}$$

or simply,

$$y^{\mathrm{m}} = y_\infty^{\mathrm{d}}\operatorname{csch}\left(\frac{\kappa h}{2}\right) \tag{5-105}$$

Likewise, we now prefer to express Π_{el} directly in terms of σ^d, and hence Equation 5-57 is the good choice, which for easy reference is written here once again,

$$\Pi_{\mathrm{el}} = \frac{(\sigma^{\mathrm{d}})^2}{2\varepsilon_0 \varepsilon}\operatorname{csch}^2\left(\frac{\kappa h}{2}\right) \tag{5-106}$$

Upon integration with respect to h, we obtain,

$$G_{\mathrm{a,el}}^{(\sigma)} = \frac{(\sigma^{\mathrm{d}})^2}{\varepsilon_0 \varepsilon \kappa}\left[\coth\left(\frac{\kappa h}{2}\right) - 1\right] \tag{5-107}$$

This is of course very different from Equation 5-61, where y^d keeps constant. In fact, only now the difference between interaction at constant potential and at constant charge in the Debye-Hückel approximation comes into play.

The relationship between the two Gibbs energies can easily be found by combination of Equations 5-61 and 5-107, and it is given by,

$$G_{\mathrm{a,el}}^{(\sigma)} = G_{\mathrm{a,el}}^{(\psi)}\coth\left(\frac{\kappa h}{2}\right) \tag{5-108}$$

Obviously, the above equations are very useful in highlighting the basic properties of interaction of diffuse double layers at constant charge. These equations are, however, poor approximations at low κh because then the required increase of surface potentials is incompatible with the Debye-Hückel approximation. In fact, the condition of fairly small y everywhere is satisfied only for particles of low and constant surface potential. For the case of constant charge interaction, the surface potentials of the particles can reach very high values at low κh, even though the potentials of the isolated particles may be quite small. Consequently, the linear PB equation is not appropriate in the constant charge case, and all the above equations should be treated with considerable reserve.

Hence, to overcome this problem, we should avoid using the linear PB equation from the very beginning for the present case. Instead, we may follow the "compression" approach to exploit the fact that conservation of the surface (diffuse) charge implies conservation of the countercharge /26/.

The midway potential

For an isolated charged plate, embedded in a symmetrical electrolyte, it is known from Equations 4-40, 4-42 and 5-54 that, at low surface potentials, the charge density drops exponentially with distance from the plate, and it can be written as,

$$\rho_\infty(x) = -2czF(zy^{\mathrm{d}}_\infty)\exp(-\kappa x) \tag{5-109}$$

where the subscript ∞ serves also as a reminder that it is for an isolated double layer.

For two parallel flat plates, a distance h apart, the total diffuse charge (originating from the two isolated plates) should remain constant in the case of interaction at constant charge. Thus, the part of charge which for isolated plates is located at distances beyond h (shaded areas in Figure 5-2) has to be accommodated between the plates. For unit area of the plates, this "accommodated" charge is given by,

$$q(h) = 2\int_h^\infty \rho_\infty \mathrm{d}x = -4czF(zy^{\mathrm{d}}_\infty)\exp(-\kappa h)/\kappa \tag{5-110}$$

Assuming that this "accommodated" charge is distributed uniformly between the plates, it will give rise to an "extra" charge density,

$$\rho'(h) = -4czF(zy^{\mathrm{d}}_\infty)\exp(-\kappa h)/(\kappa h) \tag{5-111}$$

Based on this concept, we may assume that the charge density at a point between the two interacting plates is given by the sum of the charge densities which would be produced at that point by the isolated plates plus the "extra" charge density given above. Hence, we have,

$$\rho = \rho_\infty(x) + \rho_\infty(h-x) + \rho'(h) \tag{5-112}$$

Immediately, with the help of Equations 5-109 and 5-111, we can write,

$$\rho = -2czF(zy^{\mathrm{d}}_\infty)[\exp(-\kappa x) + \exp(\kappa x)\exp(-\kappa h) + 2\exp(-\kappa h)/(\kappa h)] \tag{5-113}$$

However, for interaction in a symmetrical electrolyte, it has been known that the charge density should also follow Equation 5-37, which we write here once again,

$$\rho = -2czF\sinh(zy) \tag{5-114}$$

Thus, combination of Equations 5-113 and 5-114 yields,

$$\sinh(zy) = (zy^{\mathrm{d}}_\infty)[\exp(-\kappa x) + \exp(\kappa x)\exp(-\kappa h) + 2\exp(-\kappa h)/(\kappa h)] \tag{5-115}$$

Roughly speaking, this equation applies to any point between the plates. However, due to the assumptions we have made, it is expected that this equation estimates y fairly well only for those points at or around the mid-point between the plates.

For the midway potential, we then have,

$$\sinh(zy^{\mathrm{m}}) = 2(zy^{\mathrm{d}}_\infty)\left[\exp\left(\frac{-\kappa h}{2}\right) + \frac{\exp(-\kappa h)}{\kappa h}\right] \tag{5-116}$$

The term in square brackets is very well approximated by csch($\kappa h/2$)/2 (always better than 2%). Thus, to a good approximation,

$$\sinh(zy^{\mathrm{m}}) = zy^{\mathrm{d}}_\infty \operatorname{csch}\left(\frac{\kappa h}{2}\right) \tag{5-117}$$

This gives explicitly,

$$zy^{\mathrm{m}} = \sinh^{-1}\left[zy^{\mathrm{d}}_\infty \operatorname{csch}\left(\frac{\kappa h}{2}\right)\right] \tag{5-118}$$

The diffuse charge

By Equation 4-42, the diffuse charge σ^{d} can be determined from the isolated diffuse potential, if the latter is known, i.e.

$$\sigma^{\mathrm{d}} = -\frac{\varepsilon_0 \varepsilon \kappa RT}{F} y_{\infty}^{\mathrm{d}} \tag{5-119}$$

Otherwise, if σ^{d} is known, we should work the other way around.

The disjoining pressure

Due to the symmetry of the system under consideration, it is wise to choose the mid- point between the two plates to calculate Π_{el}. Thus, combination of Equations 5-35 and 5-117 gives, by using the relationships between hyperbolic functions /26/,

$$\Pi_{\mathrm{el}} = 2cRT\left\{\sqrt{1+\left[zy_{\infty}^{\mathrm{d}}\operatorname{csch}\left(\frac{\kappa h}{2}\right)\right]^2}-1\right\} \tag{5-120}$$

The Gibbs energy of interaction

Upon integration of Equation 5-120 with respect to h, we obtain,

$$G_{\mathrm{a,el}}^{(\sigma)} = \frac{2cRT}{\kappa}\left\{2(zy_{\infty}^{\mathrm{d}})\ln\left[\frac{B+zy_{\infty}^{\mathrm{d}}\coth(\kappa h/2)}{1+zy_{\infty}^{\mathrm{d}}}\right]-\ln\left[(zy_{\infty}^{\mathrm{d}})^2+\cosh(\kappa h)+B\sinh(\kappa h)\right]+\kappa h\right\} \tag{5-121}$$

with

$$B = \sqrt{1+\left[zy_{\infty}^{\mathrm{d}}\operatorname{csch}\left(\frac{\kappa h}{2}\right)\right]^2} \tag{5-122}$$

Comparison with the exact numerical solutions suggests that the validity of Equations 5-120 and 5-121 is excellent for $zy_{\infty}^{\mathrm{d}} \leq 2$ down to $\kappa h \sim 0.2$. However, it should be stressed that this "compression" approach is applicable only for interaction of diffuse double layers in a symmetrical electrolyte, where a very simple relationship between ρ and y is available, as in Equation 5-114. For electrolyte mixtures, this relationship becomes so complicated that the potential distribution between the two plates is hard to formulate and therefore we cannot get analytical solutions of Π_{el} and $G_{\mathrm{a,el}}$.

5.1.3 Interaction between Gouy-Stern double layers

Not much methodical thinking is needed to realize that interactions at constant potential or at constant charge are idealizations, rarely met in practice.

In fact, there are almost always Stern layers and charge redistributions, i.e. regulation almost always takes place over the diffuse part, the Stern layer and the surface upon overlap of the Gouy-Stern double layers. Thus, we may distinguish spatial and surface regulation. The former implies ion fluxes from one part of the double layer to the other; the latter only considers charge adjustment in one layer (the surface and/or the inner Helmholtz plane). The latter cannot proceed without the former.

In many situations, however, it is more likely that during a collision the charge on the surface remains essentially intact, the diffuse charge moving to the Stern layer. Hence, acting as an effective surface charge, $\sigma^0 + \sigma^{\mathrm{s}}$ is reduced. The extent to which this reduction takes place depends on the capacitances of the Stern and the diffuse layer. In this connection, the term 'capacitance' should be taken in its general meaning as indicating its purely electrical capacitance, determined by dielectric permittivities and thicknesses, and its chemical capacity, determined by ion uptake by specific binding. A Stern layer, together with the layer containing the surface charge, has a high regulation capacity when it can adsorb much charge without greatly affecting the potentials in it. The converse is true for a low regulating capacity. The ion uptake capacity is therefore determined by inner and outer Helmholtz layer capacitances, and specifically adsorbed charge σ^{s}. The chemical part of the regulation capacity is determined not only by the specific adsorption Gibbs energy of the ions, but also by the degree of occupancy θ. Stern layers for which $\sigma^s \approx \sigma^s(\text{sat})$ have a lower capacity than those for which the inner layer is almost empty. The higher the Stern layer regulation capacity is, the better the constant y^d limit is attained.

Thus, upon overlap of such layers charge and potential are both regulated, i.e. they both adjust as a function of distance h. we note that such regulation also includes adjustment of the co-ion distribution, i.e. regulation of negative adsorption.

The spatial charge regulation model

Let us now consider the following realistic situation: there is a double layer of which the surface charge σ^0 is fixed during particle encounter, either because it is strongly bound, or because it cannot desorb and escape to the bulk during the collision. Double layer overlap leads to a reduction of σ^d, which can be achieved by transporting counterions from the diffuse to the Stern layer, and hence a reduction of $\sigma^0 + \sigma^s$.

To formulate an interaction model for this case, we first assemble all the equations that we have at our disposal. For this sake, it is logical to start with the disjoining pressure, as given by Equation 5-35, because it is generally valid for symmetrical electrolytes. To make the h-dependence explicit, we had better rewrite this expression as,

$$\Pi_{\text{el}}(h) = 2cRT[\cosh zy^{\text{m}}(h) - 1] \tag{5-123}$$

Once $\Pi_{\text{el}}(h)$ is known, we can integrate to find the Gibbs energy of interaction,

$$G_{\text{a,el}}(h) = -\int_{\infty}^{h} \Pi_{\text{el}}(h')\text{d}h' \tag{5-124}$$

where h' is the integration variable. We used this equation before.

The relation $y^{\text{m}}(h)$ is rigorously available in terms of elliptical integrals, as in Equation 5-8 or 5-75. However, as we want to derive an analytical expression, we shall use Equation 5-47 instead, i.e.

$$y^{\text{m}}(h) = y^{\text{d}}(h)\,\text{sech}\left(\frac{\kappa h}{2}\right) \tag{5-125}$$

which is fairly valid when the Debye-Hückel approximation holds.

An alternative is Equation 5-11, in which we also make the h-dependence explicit to give,

$$zy^{\text{m}}(h) = 8\tanh\left[\frac{zy^{\text{d}}(h)}{4}\right]\exp\left(-\frac{\kappa h}{2}\right) \tag{5-126}$$

This expression is more restricted, because it requires the LSA approximation. In either way, we relate $y^{\text{m}}(h)$ to $y^{\text{d}}(h)$.

Next, we use Equation 5-16 to determine the diffuse charge, i.e.

$$\sigma^{\text{d}}(h) = -\left(\text{sign}y^{\text{d}}\right)\frac{2Fcz}{\kappa}\sqrt{2\left|\cosh\left[zy^{\text{d}}(h)\right] - \cosh\left[zy^{m}(h)\right]\right|} \tag{5-127}$$

where the variation of the diffuse charge with distance is now constrained by the charge balance,

$$\sigma^0 + \sigma^{\text{s}}(h) + \sigma^{\text{d}}(h) = 0 \tag{5-128}$$

where σ^0 does not depend on h by choices of conditions.

For the potential at the inner Helmholtz plane, Equation 4-99 gives, if the capacitances of the Gouy-Stern double layers are invariant with σ^0,

$$y^{\text{s}}(h) = y^0(h) - \frac{F\sigma^0}{RTC_1^s} \tag{5-129}$$

Likewise, for the diffuse potential, Equation 4-100 gives,

$$y^{\mathrm{d}}(h)=y^{\mathrm{s}}(h)-\frac{F(\sigma^{0}+\sigma^{\mathrm{s}})}{RTC_{2}^{s}}=y^{\mathrm{s}}(h)+\frac{F\sigma^{\mathrm{d}}(h)}{RTC_{2}^{s}} \tag{5-130}$$

Finally, we have the adsorption isotherm for ions at the inner Helmholtz plane, for which we have Equation 4-125, i.e.

$$\sigma^{\mathrm{s}}(h)=\frac{z_{\mathrm{j}}eN_{0}K_{\mathrm{j}}\exp(-z_{\mathrm{j}}y^{\mathrm{s}})x_{\mathrm{j}}}{1+K_{\mathrm{j}}\exp(-z_{\mathrm{j}}y^{\mathrm{s}})x_{\mathrm{j}}} \tag{5-131}$$

account for specific adsorption, if any. In the absence of specific adsorption $K_{\mathrm{j}} = 1$.

With minor changes, all of this can be modified to attain the case of constant surface potential y^0. In that case, σ^0 becomes $\sigma^0(h)$ in Equations 5-128, 5-129 and 5-130, whereas in Equation 5-129 $y^0(h)$ becomes the constant y^0.

For whatever cases, however, the set of equations have to be solved simultaneously, by which we can evaluate the potential and the charge distribution, $G_{\mathrm{a,el}}$ and Π_{el}, all as a function of h.

For the case of interaction at constant surface charge, we have found:

1. Upon overlap, the diffuse charge reduces, and even strives toward zero, implying that then the surface charge σ^0 is completely compensated by σ^{s}. The rate of this reduction is governed by both inner and outer Helmholtz layer capacitances.
2. Upon decreasing h, first y^{m} approaches y^{d}, corresponding to the disappearance of the countercharge in the diffuse layer. Thereafter, y^{d} also approaches y^{i}, whose increase eventually parallels that of y^0.
3. The Gibbs energy of interaction, $G_{\mathrm{a,el}}$, increases with increasing capacitance of the outer Helmholtz layer, due to the increase of the charge in the diffuse layer (at fixed σ^0, the capacitance of the inner Helmholtz layer is invariant).
4. As a function of K_{j}, $G_{\mathrm{a,el}}$ passes though a minimum. At low K_{j} the decrease of $G_{\mathrm{a,el}}$ at any h results from the increasing specific adsorption, which leads to a lower fraction of σ^0 that is compensated by σ^{d}. When K_{j} continues to grow, specific adsorption can become superequivalent, σ^{d} changes sign and when σ^{s} has become very strong the limiting case of interaction at constant ($\sigma^0 + \sigma^{\mathrm{d}}$) is approached.
5. The disjoining pressure has qualitatively the same features as that of the Gibbs energy of interaction.
6. Situations with constant σ^{d} or constant y^{d} apply only for large κh;

Similarly, for the case of interaction at constant surface potential, we may conclude:

1. Upon interaction, the diffuse countercharge approaches zero, some of this charge moves to the inner Helmholtz plane, the other part helps to reduce σ^0. However, the latter charge does not attain the zero value (except for $h \rightarrow 0$) because the specifically bound charges remain present and fully compensate σ^0 at very short distance.
2. The Gibbs energy of interaction $G_{\mathrm{a,el}}$ increases with increasing capacitance of the inner Helmholtz layer, because high values of this capacitance keeps y^{s} high (at fixed y^0, the capacitance of the outer Helmholtz layer is invariant).
3. The disjoining pressure has qualitatively the same features as that of the Gibbs energy of interaction.
4. Situations with constant σ^{d} or constant y^{d} apply only for large κh;

As a trend, interaction at fixed σ^0 remains stronger than that at fixed y^0, depending on parameters that have been used in the simulations.

The surface charge regulation model

Charge regulation upon overlap of double layers is the rule. The exception is that all charges remain in position with respect to the surface to which they belong. Therefore, most interaction models involve tacitly or explicitly some displacement of charge, i.e. of charge regulation. Even interaction at constant surface charge σ^0 involves spatial ionic transports, notably from the diffuse to the Stern layer. However, it may be noted that in the literature the term "charge regulation" is mostly used in a much more restricted sense, *viz.* in that σ^0 becomes $\sigma^0(h)$ because the charge forming-equilibria shift upon interaction. With this in mind, we may assume that the regulation of the surface charge is governed by a site binding mechanism (which is usually made to the case ignoring Stern layers). By this, we actually relax the condition that σ^0 or y^0 is fixed, but let these two parameters adjust themselves as a function of h, in addition to the transport across the Gouy, Stern and surface layer.

Consider now an amphoteric surface containing hydroxyl groups (ROH) that can either become negatively charged by donating a proton (leading to RO^- groups) or positively charged by adsorbing one (to form ROH_2^+). The two pertaining dissociation equilibria are characterized by the acid and base dissociation constants K_a and K_b, respectively. Hence, we have,

$$\mathrm{ROH} \Leftrightarrow \mathrm{RO^-} + \mathrm{H^+} \qquad K_\mathrm{a} = \frac{[\mathrm{RO^-}]}{[\mathrm{ROH}]} x^0_{\mathrm{H^+}} \tag{5-132}$$

and

$$\mathrm{ROH} + \mathrm{H_2O} \Leftrightarrow \mathrm{ROH_2^+} + \mathrm{OH^-} \qquad K_\mathrm{b} = \frac{[\mathrm{ROH_2^+}]\, x^0_{\mathrm{OH^-}}}{[\mathrm{ROH}]\ \ x_\mathrm{w}} = \frac{[\mathrm{ROH_2^+}]\, K_\mathrm{w}}{[\mathrm{ROH}]\ x^0_{\mathrm{H^+}}} \tag{5-133}$$

Here, the square brackets indicate surface concentration in mole m^{-2}, and the superscript 0 refers to the surface. The ion product of water K_w is dimensionless, and so are the constants K_a and K_b.

When the dimensionless potential in the surface is y^0, the surface concentration can be related to its bulk value by the Boltzmann Equation, i.e.

$$x^0_{\mathrm{H+}} = x_{\mathrm{H+}} \exp(-y^0) \tag{5-134}$$

which, in turn, can be related to the pH,

$$x_{\mathrm{H+}} = 1000 V_\mathrm{w} \exp(-2.303\mathrm{pH}) \tag{5-135}$$

where the molar volume V_w of the water enters to correct for the dimensionless problem incurred by the definition of pH.

Assuming that both positive and negative charges reside in the same plane, identified as the surface, and the number of binding sites remains infinite, the surface charge can be written as,

$$\sigma^0 = F([\mathrm{ROH_2^+}] - [\mathrm{RO^-}]) \tag{5-136}$$

Thus, from Equations 5-132, 5-133 and 5-134, we find,

$$\sigma^0 = F[\mathrm{ROH}]\left\{\frac{K_\mathrm{b} x_{\mathrm{H^+}} \exp(-y^0)}{K_\mathrm{w}} - \frac{K_\mathrm{a} \exp(y^0)}{x_{\mathrm{H^+}}}\right\} \tag{5-137}$$

At the point of zero charge (p.z.c.), we then have

$$x^{\mathrm{p.z.c.}}_{\mathrm{H^+}} = \left(\frac{K_\mathrm{a} K_\mathrm{w}}{K_\mathrm{b}}\right)^{1/2} \tag{5-138}$$

and correspondingly the pH is, with the help of Equation 5-135,

$$\mathrm{pH}^{\mathrm{p.z.c.}} = 3 + \log V_\mathrm{w} + \frac{1}{2}\Delta \mathrm{p}K + \frac{1}{2}\mathrm{p}K_\mathrm{w} \tag{5-139}$$

with

$$\Delta \mathrm{p}K = \mathrm{p}K_\mathrm{a} - \mathrm{p}K_\mathrm{b} \tag{5-140}$$

This is expected: the larger ΔpK, the lower the proton concentration must be in the solution to render the surface electroneutral. For $\Delta pK = 0$, $pH^{z.p.c.} = 7$.

Now, it is convenient to introduce the concept of the (dimensionless) Nernst potential, y^{N}, by which we may relate the surface concentration at the p.z.c. to its bulk value in a way similar to Equation 5-134, i.e. we can write,

$$x_{\mathrm{H^+}}^{\mathrm{p.z.c.}} = x_{\mathrm{H^+}} \exp(-y^{\mathrm{N}}) \tag{5-141}$$

Thus, we find,

$$y^{\mathrm{N}} = -2.303(\mathrm{pH}-\mathrm{pH}^{\mathrm{p.z.c.}}) \tag{5-142}$$

and more, combination of Equations 5-138 and 5-141 gives,

$$x_{\mathrm{H^+}} = \left(\frac{K_{\mathrm{a}}K_{\mathrm{w}}}{K_{\mathrm{b}}}\right)^{1/2} \exp(y^{\mathrm{N}}) \tag{5-143}$$

Substituting this expression into Equation 5-137 leads to,

$$\sigma^0 = F[\mathrm{ROH}]\delta \sinh(y^{\mathrm{N}}-y^0) \tag{5-144}$$

with the dissociation coefficient given by

$$\delta = 2\left(\frac{K_{\mathrm{a}}K_{\mathrm{b}}}{K_{\mathrm{w}}}\right)^{1/2} \tag{5-145}$$

It is seen that δ acts as a capacity factor: the larger its value, the higher the surface charge is at given potential, or, the less sensitive the potentials are to changes in the charge.

Had we not allowed the number of binding sites to be infinite, Equation 5-144 would have become more complicated. In that case, we have /21/,

$$\sigma^0 = F[\mathrm{ROH}]\frac{\delta \sinh\left(y^{\mathrm{N}}-y^0\right)}{1+\delta\cosh\left(y^{\mathrm{N}}-y^0\right)} \tag{5-146}$$

Obviously, σ^0 depends on h through y^0 and on pH via y^{N}; sometimes the Nernst potential y^{N} and the actual potential y^0 may be thought to have a different position.

This model can, of course, be extended to include more types of surface groups without changing the essential features of surface charge regulation. It can also be applied to the case of interaction between dissimilar surfaces, ignoring or accounting for Stern layers.

More importantly, incorporation of this kind of surface charge regulation models into the spatial charge regulation models can be done straightforwardly, by which we may study what happens in the case where σ^0 or y^0 are not fixed. In practice, it has been found that the Gibbs energy of interaction $G_{\mathrm{a,el}}$ would then become pH-dependent. At the p.z.c. it is zero, because there is no charge on the surface; the more distant pH is from $\mathrm{pH}^{\mathrm{p.z.c.}}$, the larger $G_{\mathrm{a,el}}$.

5.2 Hetero-interaction

Consider two interacting charged parallel plates, on which the two electric double layers are different. We are interested in the changes in the structures of these double layers, the Gibbs energy of interaction and the disjoining pressure, all as a function of the distance h between the two outer Helmholtz planes, i.e. the planes beyond which the countercharge is diffusely distributed. By "different" we mean that the (dimensionless) potentials y^0, y^{s} and y^{d}, and the charge densities σ^0, σ^{s} and σ^{d} may be different with respect to signs and/ or magnitudes.

5.2.1 Qualitative analysis

Qualitatively, new features may take place as compared to homo-interactions. When two surfaces with different potentials but of equal sign approach each other, the long distance interaction is always repulsive, but at short distance it may become attractive because of induction: the surface with the higher potential may impose a potential with opposite sign on the other. Whether or not in practice such a reversal takes place depends, of course, on the regulation capacities of the two Stern layers.

With interactions at fixed charge, repulsion would however always result, even though the surfaces may have charges of opposite sign.

When two unequal double layers overlap a variety of phenomena can occur, determined by the two surface potentials y_1 and y_2, and/or surface charges σ_1 and σ_2 and the ways in which the two charge distributions regulate. As in homo-interactions, the overlap takes primarily place between the two diffuse double layer parts, with the boundary conditions $y_1^{d}(s)$, $y_2^{d}(s)$, $\sigma_1^{d}(s)$ and $\sigma_2^{d}(s)$ depending on the regulation capacities of the two surfaces and the two Stern layers. When these capacities are large, much charge can be retained in the non-diffuse parts without significant change of y^{d}; in the limit of infinite regulation capacity, the case of "constant diffuse potential" is attained. In the opposite limit the case of "constant diffuse charge" is approached. Hence, systems can be imagined in which one of the two double layers behaves as "quasi-constant potential", the other as "quasi-constant charge".

As compared with homo-interactions the other new element is the asymmetry of the potential profile between the two surfaces. The minimum potential is no longer located at the half-distance but shifted towards the surface with the lower y^{d}. In some situations the minimum even disappears completely as a result of induction, and then attraction prevails.

In passing it is noted that something similar can also happen between two double layers that are identical with respect to their charges and potentials at large distance, but which have surfaces of different regulation capacities.

5.2.2 Quantitative analysis

Anticipating quantitative analysis, we may state that for interaction between dissimilar double layers the potentials or charges of the lower-charged surface are more critical than those of the higher-charged one. This is a consequence of the tendency of diffuse double layers to accommodate most of their charges in the part where the potentials are high, i.e. close to the outer Helmholtz planes.

In principle, as for homo-interaction, there are two ways at our disposal to quantify the hetero-interaction:

1. Solve the Poisson-Boltzmann Equation; find the Gibbs energy by an appropriate charging procedure; subtract the Gibbs energy for the two double layers far apart, finding the Gibbs energy of interaction; upon differentiation of $G_{a,el}$ with respect to h gives the disjoining pressure.
2. Start with the disjoining pressure; use the Poisson-Boltzmann Equation to find the minimum potential; integration provides then the Gibbs energy of interaction.

If we follow the first route, Equation 5-4 would also remain valid for the present case for symmetrical electrolytes, which for easy reference we write here once again,

$$\left(\frac{\mathrm{d}y}{\mathrm{d}x}\right)^2 = \frac{2\kappa^2}{z^2}\left[\cosh(zy) + C\right] \tag{5-147}$$

However, establishing the integration constant C is now slightly more complicated than for homo-interactions, and in fact several options are available.

The integration constant

For cases with a minimum potential y^{m}, we would still have,

$$C = -\cosh(zy^{m}) \tag{5-148}$$

The difference, as compared with homo-interactions, is that the position x^{m} does not coincide with $h/2$ any more.

For cases without a minimum potential, the derivative of the potential at the point of zero potential could be used to evaluate C, i.e. we can write,

$$C = \frac{z^2}{2\kappa^2}\left(\frac{\mathrm{d}y}{\mathrm{d}x}\right)^2_{y=0} - 2 \qquad (5\text{-}149)$$

Alternatively, we can determine C by relating the field strength at $x = 0$ and $x = h$ to the corresponding diffuse charges, using Equations 5-1 and 5-2, which are now written as,

$$\left(\frac{\mathrm{d}y}{\mathrm{d}x}\right)^2_{x=0} = \left(\frac{\sigma_1^{\mathrm{d}} F}{\varepsilon_0 \varepsilon RT}\right)^2 \qquad (5\text{-}150)$$

and

$$\left(\frac{\mathrm{d}y}{\mathrm{d}x}\right)^2_{x=h} = \left(\frac{\sigma_2^{\mathrm{d}} F}{\varepsilon_0 \varepsilon RT}\right)^2 \qquad (5\text{-}151)$$

Hence, the third pair of solutions is,

$$C = \frac{1}{2}\left(\frac{\sigma_1^{\mathrm{d}} zF}{\varepsilon_0 \varepsilon \kappa RT}\right)^2 - \cosh\left(zy_1^{\mathrm{d}}\right) = \frac{1}{2}\left(\frac{\sigma_2^{\mathrm{d}} zF}{\varepsilon_0 \varepsilon \kappa RT}\right)^2 - \cosh\left(zy_2^{\mathrm{d}}\right) \qquad (5\text{-}152)$$

This equation offers, at the same time, a relationship between y_1^{d}, σ_1^{d}, y_2^{d} and σ_2^{d}.

The disjoining pressure

If we follow the second route, Equation 5-33 can also be obtained for the present case, which is now written as,

$$\Pi_{\mathrm{el}} = cRT\left[2\cosh(zy) - \frac{z^2}{\kappa^2}\left(\frac{\mathrm{d}y}{\mathrm{d}x}\right)^2 - 2\right] \qquad (5\text{-}153)$$

Combining this with Equation 5-147 yields,

$$\Pi_{\mathrm{el}}\,(h) = -2cRT\left[C(h) + 1\right] \qquad (5\text{-}154)$$

where we have made the h-dependence explicit.

Phenomenologically, this final equation is simple and general but the elaboration is not. We see that the sign of Π_{el} depends on C; it may change as a function of h. $\Pi_{\mathrm{el}}(h)$ is repulsive if $C < -1$, it is attractive for $C > -1$. On the basis of diffuse double layer theory only, it is virtually impossible to discriminate between the various options of repulsion and attraction, because the sigh of Π_{el} is sensitive to the extent of constancy of y_1^{d}, y_2^{d}, σ_1^{d} and σ_2^{d} upon interaction. The resilience of these crucial parameters against the action of the double layer of the second particle is determined by the two primary (spatial and planar) regulation capacities. For these, no simple general rules can be given, although several advanced partial solutions can be found in the literature.

Approximate analytical solutions

As shown previously for homo-interaction, the Debye-Hückel approximation often gives a rapid approximate result. For hetero-interaction between two parallel flat plates with constant diffuse potentials, the following equation, derived by Hogg et al. /27/, has become popular,

$$G_{\mathrm{a,el}}^{(\psi)} = \frac{\varepsilon_0 \varepsilon \kappa}{2}\left(\frac{RT}{F}\right)^2 \left\{\left[(y_1^{\mathrm{d}})^2 + (y_2^{\mathrm{d}})^2\right]\left[1 - \coth(\kappa h)\right] + 2y_1^{\mathrm{d}} y_2^{\mathrm{d}} \mathrm{csch}(\kappa h)\right\} \qquad (5\text{-}155)$$

The practicality of this equation stems from the fact that only the two ζ-potentials are needed. It should describe weak overlap fairly well, but of course does not suffice to predict the low κh behaviour.

For plates of equal potentials, Equation 5-155 reduces to Equation 5-61. Now the typical difference between homo-interaction and hetero-interaction arises if we compare the forms of these two equations. In the former case the interaction can always be written as a product $f(y^{\mathrm{d}}) \times g(\kappa h)$, in the latter this is no longer the case, except at large κh. This new behaviour is directly correlated with the propensity of sign reversal.

By differentiation of Equation 5-155 with respect to *h*, we obtain,

$$\Pi_{\mathrm{el}}^{(\psi)}=\frac{\varepsilon_0\varepsilon}{2}\left(\frac{\kappa RT}{F}\right)^2\left\{\left[(y_1^{\mathrm{d}})^2+(y_2^{\mathrm{d}})^2\right]\mathrm{csch}^2(\kappa h)-2y_1^{\mathrm{d}}y_2^{\mathrm{d}}\mathrm{csch}(\kappa h)\coth(\kappa h)\right\} \tag{5-156}$$

The constant charge equivalent of Equation 5-115 is also available and it reads /28/,

$$G_{\mathrm{a,el}}^{(\sigma)}=\frac{\varepsilon_0\varepsilon\kappa}{2}\left(\frac{RT}{F}\right)^2\left\{\left[(y_1^{\mathrm{d}})^2+(y_2^{\mathrm{d}})^2\right]\left[\coth(\kappa h)-1\right]+2y_1^{\mathrm{d}}y_2^{\mathrm{d}}\mathrm{csch}(\kappa h)\right\} \tag{5-157}$$

The difference with the constant potential equivalent is only in the sign of the first term in the curly brackets.

Correspondingly, we have,

$$\Pi_{\mathrm{el}}^{(\sigma)}=\frac{\varepsilon_0\varepsilon}{2}\left(\frac{\kappa RT}{F}\right)^2\left\{\left[(y_1^{\mathrm{d}})^2+(y_2^{\mathrm{d}})^2\right]\mathrm{csch}^2(\kappa h)+2y_1^{\mathrm{d}}y_2^{\mathrm{d}}\mathrm{csch}(\kappa h)\coth(\kappa h)\right\} \tag{5-158}$$

This expression has been shown to be reasonably good in describing the interactions between oppositely charged plates, because where the potentials between the plates are not very great. It is, however, a poor approximation in other cases, especially at close approach of the two plates, because then the required increase of surface potentials is incompatible with the Debye-Hückel approximation.

To improve this pair, the "compression" approach could of course be followed to treat hetero-interaction at constant charge. By this route, for very special cases where only one symmetrical electrolyte is considered in the Debye-Hückel approximation, Gregory /26/ found,

$$\Pi_{\mathrm{el}}^{(\sigma)}=cRT\left[2B-(zy_{1\infty}^{\mathrm{d}}-zy_{2\infty}^{\mathrm{d}})^2\exp(-\kappa h)/B^2-2\right] \tag{5-159}$$

with

$$B=\sqrt{1+\left[\frac{zy_{1\infty}^{\mathrm{d}}+zy_{2\infty}^{\mathrm{d}}}{2}\mathrm{csch}\left(\frac{\kappa h}{2}\right)\right]^2} \tag{5-160}$$

For plates of equal potentials, Equation 5-159 reduces to Equation 5-120.

Comparison with exact numerical solutions suggests that Equation 5-159 gives much better results under most conditions, as compared to Equation 5-158. The exception is when the charges on the plates are opposite in sign and equal (or nearly so) in magnitude. The reason for this is that the second term on the r.h.s. of Equation 5-159 is not a good representation of the attractive component of the force between the two plates. However, when the plate potentials are not greatly different, this term is very much smaller than the first and the inaccuracy is not apparent. When the potentials are equal and opposite, the first and the third terms cancel out and the inadequacy of the second is then most noticeable. When the plate potentials are of the same sign, the second term is small enough to be neglected, and then integration is more easily carried out; this gives,

$$G_{\mathrm{a,el}}^{(\sigma)}=\frac{2cRT}{\kappa}\left\{2(z\bar{y})\ln\left[\frac{B+z\bar{y}\coth(\kappa h/2)}{1+z\bar{y}}\right]-\ln\left[(z\bar{y})^2+\cosh(\kappa h)+B\sinh(\kappa h)\right]+\kappa h\right\} \tag{5-161}$$

with

$$\bar{y}=\frac{1}{2}(y_{1\infty}^{\mathrm{d}}+y_{2\infty}^{\mathrm{d}}) \tag{5-162}$$

Note that Equation 5-159 applies only when the potentials of the isolated particles are fairly small (y^{d} < 2) down to κh ~ 0.2.

In addition, it should be added that a wealth of equations for $G_{\mathrm{a,el}}$ for different situations of hetero-interaction has been derived by McCormack et al. /29/; several of these contain elliptic integrals. However, the most commonly used expression is the one resulted from the linear superposition approximation for symmetrical electrolytes, and it reads,

$$G_{\mathrm{a,el}} = \frac{64cRT}{\kappa}\tanh\left(\frac{zy_{1\infty}^{\mathrm{d}}}{4}\right)\tanh\left(\frac{zy_{2\infty}^{\mathrm{d}}}{4}\right)\exp(-\kappa h) \tag{5-163}$$

This equation works fairly well for weak overlap for hetero-interactions, and in practice it applies to both cases, either at constant potential or at constant charge.

Correspondingly, we have,

$$\Pi_{\mathrm{el}} = 64cRT\tanh\left(\frac{zy_{1\infty}^{\mathrm{d}}}{4}\right)\tanh\left(\frac{zy_{2\infty}^{\mathrm{d}}}{4}\right)\exp(-\kappa h) \tag{5-164}$$

For plates of equal potentials, this equation reduces to Equation 5-39.

6 Solvent structure-mediated interactions

Basically, the structure of a liquid adjacent to a hard wall differs from that in bulk. Layering takes place, extending over a very few molecular layers, resulting in a density distribution normal to the surface $\rho_N(x)$ displaying oscillations which decay rapidly with x. This is a general phenomenon, observed for hydrophilic and hydrophobic surfaces. The origin is the short-distance molecular repulsion.

When two such surfaces approach to such short distance that these structured zones (the liquid layers adjacent to the two boundaries) overlap, work has to be done by or on the system to change them, giving rise to solvent structure-mediated interactions.

At extremely short distances these interactions are oscillating, the maxima and minima being determined by the matching of the strong oscillations, i.e., they are alternatively repulsive and attractive. For somewhat longer distance, it has been found empirically that the decay is of an exponential nature, i.e. the disjoining pressure due to the solvent structure-mediated interaction between two hard flat surfaces; a distance s apart; can be given by /30/,

$$\Pi_{str} = K_{str} \exp(-s/\lambda) \tag{6-1}$$

where K_{str} is a proportionality constant characterizing the strength of interaction and λ is a measure of the structure decay as a function of distance. The latter is typically short-range, only around a few nanometers.

This expression holds at $s \geq \lambda$, and the distance $s = h + 2d$ if we take the Stern layer with a thickness d into account.

Upon integration of Equation 6-1 with respect to s, we obtain the Gibbs energy of the solvent structure-mediated interaction, as given in Equation 1-5, i.e.

$$G_{a,str} = K_{str} \lambda \exp(-s/\lambda) \tag{6-2}$$

Hence, by means of the Derjaguin approximation for a cylinder of length l and radius a interacting with a semi-infinite plate at short distances, we arrive at /31/,

$$\Pi_{str} = K_{str} l \sqrt{2\pi\lambda a} \exp(-s/\lambda) \tag{6-3}$$

and correspondingly,

$$G_{str} = K_{str} \lambda l \sqrt{2\pi\lambda a} \exp(-s/\lambda) \tag{6-4}$$

Likewise, for two interacting cylinders of equal radius of a, we have,

$$\Pi_{str} = K_{str} l \sqrt{\pi\lambda a} \exp(-s/\lambda) \tag{6-5}$$

and,

$$G_{str} = K_{str} \lambda l \sqrt{\pi\lambda a} \exp(-s/\lambda) \tag{6-6}$$

7 Extended DLVO theory

Traditional DLVO theory considers electrostatic repulsion and Van der Waals attraction as the sole, and additive, contributions to pair interaction. The theory is elaborated for flat and spherical symmetries, and it mostly assumes purely diffuse double layers at fixed potential and non-retarded Van der Waals forces. With this DLVO model, a number of important observations could be accounted for, at least semiquantitatively. These include:

1. the very strong influence of the valency of the counterion (the Schulze-Hardy rule);
2. the relationship between stability and the ζ-potential;
3. the rate of coagulation;
4. weak secondary minimum coagulation for big particles, leading to shear thinning and thixotropy.

All of this has supported the essential correctness of the model. However, over the half century after its publication, it transpired that a number of (mostly quantitative) defects required systematic consideration. These mainly include:

1. Double layers are not purely diffusive. Only a small but very relevant fraction of the countercharge, depending on the nature of the indifferent electrolyte and its concentration, resides in the diffuse part.
2. It follows from the above that the surface potential occurring in the DLVO model must be replaced by the potential of the diffuse double layer, and likewise, the surface charge by the diffuse charge.
3. Counterion specificity is caused by the specific adsorption in the Stern layer. The phenomenon of lyotropic series is essentially absent in DLVO theory.
4. Van der Waals (dispersion) forces have to be corrected for retardation, except at short distances.
5. The presence of a Stern layer results in Van der Waals forces operating over a longer interaction distance compared to those in the diffuse layer, i.e. $s = h + 2d$, where h is the distance between the two outer Helmholtz planes and d the Stern layer thickness.
6. At very short distances, solvent structure-mediated forces have to be added.
7. In the DLVO theory, the double layers are assumed to be continually equilibrated.

Thus, a variety of improvements can be made to the DLVO theory /21/; leading to the development of extended DLVO models which we abbreviate as DLVOE for the sake of distinction. Basically, as compared to classical DLVO theory, DLVOE covers a number of phenomena that are quite common in practice, and which go far beyond the Poisson-Boltzmann level. These additional phenomena include ion size effects, non-electrostatic (specific) adsorption, and the effect of ions and surfaces on the structure of water. The shortcut to keep all these features tractable was to account for them only in the Stern layer that is the layer where they dominate. A further advantage is that diffuse theory is only needed for that part of the double layer where the Poisson-Boltzmann premises hold. For this part we can fall back on DLVO, with the improvement that $y^{d}(h)$ follows from regulation. One may perhaps generalize the difference between DLVO and DLVOE in that the former is essentially electrostatic, whereas the latter also exposes the chemistry in the wide sense.

7.1 Potential energy curves

Throughout the DLVOE theory /21/, G_{el}, G_{VdW} and G_{str} are considered to be additive, whereas the surfaces are assumed to be molecularly flat and free of surfactants. Then, the general shape of DLVOE interaction curves may be sketched and shown in Figure 7-1.

In the top picture, the Gibbs energy of interaction is given. For two semi-infinite parallel plates this is expressed in J m^{-2}, for two spheres and other finite objects it is in J. The lower picture gives the derivative, which for plates is the disjoining pressure Π, in N m^{-2}, and for two spheres etc is the force f, in N. The extremes in $G(h)$ corresponding to zero values in $\Pi(h)$ or $f(h)$, whereas the extremes in the latter are found at the binding points in the Gibbs energy $G(h)$. On the other hand, the occurrence, heights,

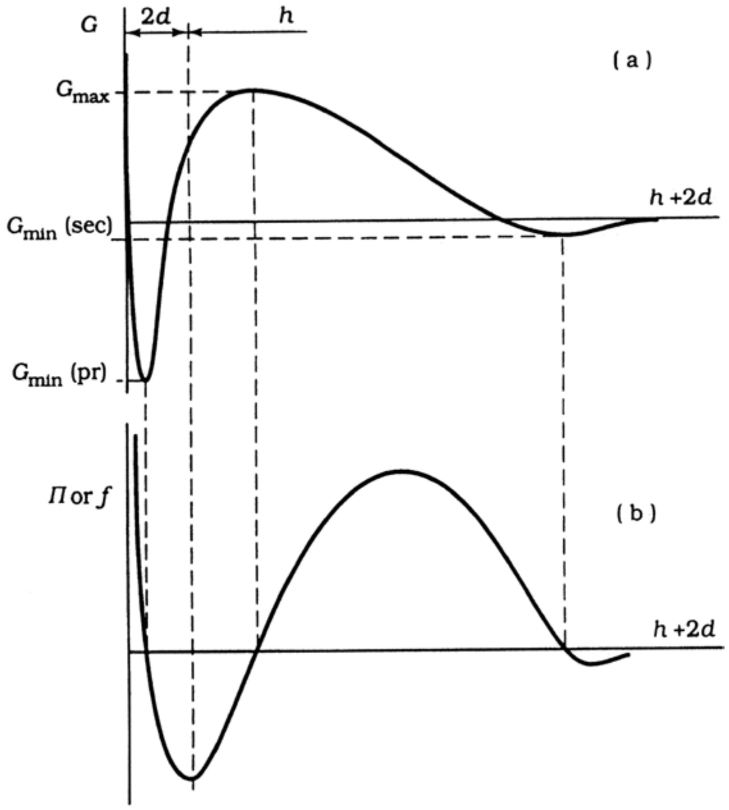

Figure 7-1. *General nature of DLVOE homo-interaction curves. Top, Gibbs energy; bottom, disjoining pressure or force. The distance between the two surfaces is h + 2d.*

and shapes of these maxima and minima depend on the magnitudes of the constituting contributions (G_{el}, G_{VdW} and $G_{solv,str}$), and hence on the salt concentration c_{salt}, the pH, the radius a etc.

General features

Qualitatively, G and Π exhibit the same extrema, but those for Π are systematically at larger h.

Starting at large $h + 2d$, first the shallow secondary minimum is observed. The reason for its existence is that for large distance, G_{el} decays as $e^{-\kappa h}$, which for large κ is steeper than the decay of G_{VdW}. For low κ, G_{el} extends so far that the secondary minimum then becomes invisible.

For big spherical particles where $h << a$, G_{VdW} decays as $(h+2d)^{-1}$, i.e.

$$G_{VdW}(h) = -\frac{A_{11}}{12(h+2d)} \tag{7-1}$$

For smaller particles at large distance, however, the decay of G_{VdW} is,

$$G_{VdW}(h) = -\frac{A_{11}}{6}\left\{\frac{2a^2}{(h+2d)^2+4a(h+2d)} + \frac{2a^2}{(h+2d)^2+4a(h+2d)+4a^2} + \ln\left[\frac{(h+2d)^2+4a(h+2d)}{(h+2d)^2+4a(h+2d)+4a^2}\right]\right\} \tag{7-2}$$

and hence it is steeper. Moreover, retardation sets in which also weakens G_{VdW} at large distance. Together with the fact that G_{el} and G_{VdW} both increase with the radius a (as a first approximation both linearly), we arrive at the conclusion that the depth of the secondary minimum G_{min}(sec) decreases with decreasing particle size. In fact, for low a, it effectively disappears and therefore it is virtually impossible to coagulate nanoparticles in the secondary minimum.

The repulsive maximum, $G_{\max}$, is of course caused by diffuse double layer overlap. It is commonly called the energy barrier. This term is sloppy, because to a large extent it is entropically determined, *viz*. by the diffuseness and regulation of charges upon overlap.

When the barrier is high enough, it can stabilize a sol. Semiquantitatively, the probability that an encounter between two particles leads to coagulation decays as $\exp(-G_{\max}/k_BT)$, where $G_{\max}$ acts as the activation (Gibbs) energy. Barriers with $G_{\max} \sim k_BT$ (which is the unit of thermal energy) offer no protection against coagulation, whereas those for $G_{\max} \geq 10–15\ k_BT$ ensure stability for most practical purposes. In between a range from rapid to increasingly slow coagulation with decreasing salt concentration c_{salt} is found. Although there is no sharp transition between "stable" and "unstable" sols, there are methods of determining rather reproducible critical coagulation concentrations.

On the other hand, to create an energy barrier there must be a distance range over which G_{el} exceeds G_{VdW}. This is only possible for low c_{salt}, because only then does G_{el} decay slowly enough to outweigh G_{VdW}, as we can see from the following expression of G_{el} for interaction of two spherical particles of equal radius a,

$$G_{\text{el}}^{(\psi)} = \frac{64\pi acRT}{\kappa^2}\tanh^2\left(\frac{zy^{\text{d}}}{4}\right)\ln\left(1+e^{-\kappa h}\right) \qquad (7\text{-}3)$$

It must be stressed that the range of action of G_{el} is at least as relevant as its absolute magnitude. Typically, for $h \rightarrow 0$, as in Equation 7-3, $G_{\text{el}} \sim c_{\text{salt}}/\kappa^2$, which is independent of c_{salt}.

When two particles can overcome the energy barrier, they can approach each other until they reach the primary minimum (the distance where the primary minimum is located will be close to $h = 0$, implying that it is equal to about twice the Stern thickness), giving rise to primary minimum coagulation. Depending on d (the Stern layer thickness), this minimum can be deep and narrow, and it is mainly determined by the counteraction between G_{VdW} and G_{str}.

An interesting issue here is weather primary minimum coagulation can be reversed, say by removing the electrolyte (secondary minimum coagulation usually is; sols, coagulated in the secondary minimum are shear thinning, if not thixotropic). Stated otherwise, can such coagulated system repeptize by removing the electrolyte? The reply to this question depends to a large extent on the possibility of leaching the electrolyte from the gap, and the ensuing inner-layer regulation.

Knowing these general features of DLVOE interaction curves, we shall now explore the influence of some variables in greater detail. The aim is to obtain a quantitative feeling for the effect of some relevant system parameters. To restrict the number of variables we shall only consider spherical particles, and forget G_{str} for the moment. Hence, the total Gibbs energy of interaction can be written as, for the case of constant ψ^{d},

$$G_{\text{tot}}(h) = G_{\text{el}}^{(\psi)}(h) + G_{\text{VdW}}(h) \qquad (7\text{-}4)$$

Influence of the Hamaker constant

Upon increasing A_{11}, the height of the energy barrier decreases, whereas the depth of the secondary minimum increases. In fact, of the various parameters in Equations 7-2 and 7-3, the effective Hamaker constant A_{11} is the one over which we have least control; its value is determined by the chemical nature of the dispersed and continuous phases. The presence of a small amount of colloids in the continuous phase leads, however, only to a negligible alternation of the value of A_{11} for the solvent.

Influence of the retardation

Retardation becomes significant only at large distances and only when the value of G_{tot} is more critical. Its effect would be negligible in cases where either G_{el} or G_{VdW} prevails everywhere.

Influence of the diffuse potential

The height of the energy barrier increases with increasing values of the diffuse potential, y^{d}, as might be expected in view of the increase of repulsion with this quantity. For large values of y^{d}, the hyperbolic tangent in Equation 7-3 goes nearly to unity, so sensitivity of the total interaction energy, G_{tot}, to the value of y^{d} decreases as y^{d} increases.

Influence of the Stern layer thickness

The height of the energy barrier increases with increasing the Stern layer thickness d. In extreme cases where the position of the energy barrier is such that G_{VdW} is in its steeper part, $G_{\max}$ may increase by a factor of more than two between $d = 0$ and $d = 0.3$ nm. It is unlikely that d is much larger than 0.3 nm (that would require very thick hydrated layers, which have never been proven for hydrophobic surfaces without steric interaction).

Thus, traditional DLVO theory inherently with $d = 0$ underestimates G_{tot} because at the position of the maximum G_{VdW} is lower than was thought.

The position of the maximum is, however, only slightly affected by the thickness d.

Influence of the particle radius

Upon increasing the particle radius a, the repulsive part of G_{tot} becomes more positive, the attractive part more negative. G_{tot} is therefore not exactly proportional to a, as would be predicted by simplified short-distance approximations.

Influence of the electrolyte concentration and valency

Of various quantities which affect the shape of the potential energy curves, none is as accessible to empirical adjustment as κ. This quantity depends on both the concentration and valency of the indifferent electrolyte, and so does the diffuse potential ψ^{d} (which has been used in DLVOE instead of ψ^{0} in DLVO).

For κ, we can write, by Equation 4-59,

$$\kappa^2 = \text{const. } cz^2 \tag{7-5}$$

whereas for ψ^{d}, an empirical formula can be used,

$$\psi^{\mathrm{d}} \approx \zeta = \text{const.} c^{-1/4} z^{-2} \tag{7-6}$$

Thus, with the Debye-Hückel approximation holds, Equation 7-3 immediately gives,

$$G_{\mathrm{el}}^{(\psi)} \propto c^{-1/2} z^{-4} \tag{7-7}$$

As a result, it is evident that the height of the energy barrier, $G_{\max}$, decreases very rapidly with increasing c_{salt} and the valency of the counterion, and the latter effect is much more prominent than the former; this illustrates qualitatively the Schulze-Hardy rule for the critical coagulation concentration (c.c.c.) which we will discuss in detail in the following subsection. At this stage, however, it should be pointed out that the c.c.c. is much higher when a Stern layer is involved than otherwise.

7.2 The c.c.c. and the Schulze-Hardy rule

The c.c.c. is, by definition, the indifferent electrolyte concentration below which a sol is stable and above which it is unstable. Although there is no sharp transition between "stable" and "unstable" sols, there are methods for determining c.c.c. experimentally. Among these, the coagulation series method involves a series of vials, containing a fixed amount of sol, and adding increasing amount of electrolyte to establish the concentration above which sedimentation of aggregated particles becomes clearly visible after a preset time. This method includes also stirring and/or shaking steps with the purpose of making coagulation as efficient as possible, essentially combining perikinetics with orthokinetics. In this way, fairly sharp borderlines between "stable" and "unstable" sols are obtainable.

Alternatively, the rate of coagulation method may be used, in which this rate is mostly measured optically as a function of c_{salt}. Plots of $\log W$ (here, W is a standardized measure of the probability that a pair encounter leads to aggregation) against $\log c_{\mathrm{salt}}$ consist of a descending and a horizontal branch, whose intersection is identified as the c.c.c.

In practice, both methods show the same trends with respect to valency and nature of the electrolyte, although for the rate-method, c.c.c. values are higher by about 30–60%. This phenomenon suggests that the electrolyte behaves as if it is not equally efficient in these methods, and thus there is a method-specific threshold discriminating between stability and instability, say $G_{\max} = bk_{\mathrm{B}}T$.

Coagulation by a single electrolyte

Analytical analyses can be made to find approximate relationships between c.c.c. and z if only a single electrolyte is involved in the system, i.e. to account quantitatively for the Schulze-Hardy rule. For this purpose, we shall use the fact that the disjoining pressure Π becomes zero at $G_{\max}$. It should, however, be noted that most of our equations apply for symmetrical (z-z) electrolytes, but as the co-ions are negatively adsorbed their role is minor, and so we may interpret z as the valency of the counterion.

Consider now the case where the particles are not too small, i.e. $(h_{\max}+2d) << a$, so that Equation 7-1 may be used instead of 7-2. Then, we can write,

$$G_{\mathrm{tot}} = \frac{64\pi acRT}{\kappa^2}\tanh^2\left(\frac{zy^{\mathrm{d}}}{4}\right)\ln\left(1+e^{-\kappa h}\right) - \frac{A_{11}a}{12(h+2d)} \tag{7-8}$$

For mathematical convenience, we may replace $\ln(1+e^{-\kappa h})$ by $0.693e^{-\kappa h}$, which is a good approximation. This leads to,

$$G_{\mathrm{tot}} = \frac{44.36\pi acRT}{\kappa^2}\tanh^2\left(\frac{zy^{\mathrm{d}}}{4}\right)\exp(-\kappa h) - \frac{A_{11}a}{12(h+2d)} \tag{7-9}$$

Thus, upon differentiation with respect to h, we obtain,

$$\Pi = \frac{44.36\pi acRT}{\kappa}\tanh^2\left(\frac{zy^{\mathrm{d}}}{4}\right)\exp(-\kappa h) - \frac{A_{11}a}{12(h+2d)^2} \tag{7-10}$$

On setting $\Pi = 0$ in this equation, the distance $h_{\max}$ at which G_{tot} becomes the repulsive maximum $G_{\max}$ is obtainable, i.e. we have,

$$\frac{44.36\pi acRT}{\kappa}\tanh^2\left(\frac{zy^{\mathrm{d}}}{4}\right)\exp(-\kappa h_{\max}) = \frac{A_{11}a}{12(h_{\max}+2d)^2} \tag{7-11}$$

and,

$$G_{\max} = \frac{44.36\pi acRT}{\kappa^2}\tanh^2\left(\frac{zy^{\mathrm{d}}}{4}\right)\exp(-\kappa h_{\max}) - \frac{A_{11}a}{12(h_{\max}+2d)} \tag{7-12}$$

Hence, combination of these two equations yields,

$$G_{\max} = \frac{A_{11}a}{12\kappa(h_{\max}+2d)^2} - \frac{A_{11}a}{12(h_{\max}+2d)} \tag{7-13}$$

This equation may be called the implicit DLVOE expression for $h_{\max}$. It can be compared with that of the DLVO theory, which sets $G_{\max} = 0$ and $d = 0$. Hence, the DLVO theory gives,

$$\kappa h_{\max} \approx 1 \qquad \text{(DLVO)} \tag{7-14}$$

The DLVOE theory takes, however, the Stern layer into account, and thus if $G_{\max} = 0$ is also set as a threshold, we have,

$$\kappa(h_{\max} + 2d) \approx 1 \qquad \text{(DLVOE)} \tag{7-15}$$

This expression suggests that the maximum is situated not far beyond twice the Stern layer thickness, and because of the $2d$ effect, $h_{\max}$ is less dependent on c_{salt} than in the DLVO theory. The physical prediction is that, as soon as two particles have overcome the maximum, solvent structure-mediated interaction takes over so that there is little or no room for a primary minimum. In order to find such a minimum, $G_{\max}$ should be low; i.e. electrostatic stabilization must be suppressed.

Equation 7-15 can be re-substituted into Equation 7-11, yielding,

$$\frac{16.32\pi cRT}{\kappa}\tanh^2\left(\frac{zy^{\mathrm{d}}}{4}\right)\exp(2\kappa d)=\frac{A_{11}\kappa^2}{12} \tag{7-16}$$

where c = c.c.c. Basically, this equation therefore comes down to a definition of the c.c.c. in terms of y^{d}, A_{11} and d.

At this point, we shall recall the Schulze-Hardy rule, an empirical rule that is generally valid for hydrophobic colloids. It states that the stability decreases very strongly with the valency of the counterion. To explain this rule quantitatively, the DLVO theory invokes an expression similar to Equation 7-16 with $d = 0$ and $y^{\mathrm{d}} \rightarrow y^0$. Hence, for the spherical particles we considered, DLVO theory would have written,

$$\frac{16.32\pi cRT}{\kappa}\tanh^2\left(\frac{zy^{0}}{4}\right)=\frac{A_{11}\kappa^2}{12} \tag{7-17}$$

It follows immediately from Equation 4-59 that,

$$\text{c.c.c.} = \text{const.}\frac{\tanh^4(zy^0/4)}{A_{11}^2 z^6} \tag{7-18}$$

with

$$\text{const.} = (195.84\pi RT)^2\left(\frac{\varepsilon_0\varepsilon RT}{2F^2}\right)^3 \tag{7-19}$$

As y^0 was supposed to be high, the hyperbolic tangent in Equation 7-18 goes to unity, so that the DLVO theory concludes:

$$\text{c.c.c} \propto z^{-6} \tag{7-20}$$

In the DLVOE theory, however, the relationship is much more complicated, and actually an important improvement of the interpretation of the Schulze-Hardy rule is already obtained by replacing y^0 with y^{d}. Taking only the first term of the series expansion of the hyperbolic tangent in Equation 7-21, we would then arrive at,

$$\text{c.c.c} = \frac{\text{const.}}{256}\frac{(y^{\mathrm{d}})^4}{A_{11}^2 z^2}\exp(4\kappa d) \tag{7-21}$$

This expression implies that the relationship between c.c.c. and z depends on the way in which y^{d} changes with these variables, and this will depend on the system conditions such as the pH and the nature of the electrolyte. The particle radius has, however, no influence on the c.c.c. values for the short-distance case under consideration.

Assuming that the system obeys Equation 7-6, the above equation gives,

$$\text{c.c.c} \propto z^{-5} \tag{7-22}$$

In addition, a number of secondary phenomena can now also be accounted for, such as ion specificity: under otherwise fixed conditions, stronger counterion adsorption results in a lower y^{d}, and because of the 4th power this propagates very strongly in the c.c.c. values.

Coagulation by electrolyte mixtures

The influence of mixed counterions is a rather subtle phenomenon: if counterion 1 has a certain coagulation propensity and counterion 2 a higher one, is a 50–50 mixture then 50/50 effective, or more so, or less? Figure 7-2 shows the various possibilities that have been considered for salt mixtures. This figure should be read as follows: starting from pure salt 2, experiments are carried out with 90%, 80% … etc of c.c.c.–2, where the concentration of salt 1 (as a fraction of c.c.c.–1) is established to achieve coagulation.

Only when c.c.c.–1 = c.c.c.–2 may additivity be expected. This is the least interesting case. More generally the two c.c.c.'s are different, especially so when the counterions have different valencies, or very different specific adsorption Gibbs energies. For the latter case, we may consider in the framework of DLVOE theory that, for a particle of fixed surface charge, the charge distribution over the two competing counterions at the inner Helmholtz plane will be determined by an ion exchange mechanism. For $z_1 = z_2$, we then have,

$$\frac{\sigma_1^{\mathrm{s}}}{\sigma_2^{\mathrm{s}}} = K_{1,2}\frac{c_1}{c_2} \qquad (7\text{-}23)$$

with

$$K_{1,2} = \exp[-(\Delta_{\mathrm{ads}}G_1 - \Delta_{\mathrm{ads}}G_2)/\mathrm{RT}] \qquad (7\text{-}24)$$

According to this rule, the Stern layer is, over the entire concentration range, richer in the more strongly specifically adsorbing ion, leading to a higher coagulation propensity, or to a lower c.c.c. with synergism as the generally expected result.

For systems of fixed surface potential, the situation is more subtle because then σ^0 can vary over the range. In fact, experimental studies suggest that in some cases synergism is found but in other cases superadditivity shows up /21/.

Overcharging – charge reversal

Overcharging is the phenomenon in which more countercharge adsorbs than is required for compensation of the surface charge. As a result, the ζ-potential inverts its sign, hence the name charge reversal. However, this term is sloppy because the surface charge does not reverse its sign. On the contrary, its absolute value increases because of the increased screening. For colloid science overcharging is an immensely important phenomenon, and it is mostly achieved by the more powerful adsorption of ionic surfactants and poly-electrolytes. It is a means of controlling the sign of y^{d} or σ^{d} and, in this way, controlling the sign of the counterions to which the c.c.c. is very sensitive.

As long as the surface charge is smeared out, overcharging can only occur if counterions absorb superequivalently and this can happen only when they have a specific attraction for the surface, i.e. a chemical attraction in addition to the Coulombic one.

There is much empirical information on superequivalency and overcharging, but only some of it is obtained under sufficiently well-defined conditions (pH, c_{salt}, effect of the adsorbent) to be helpful to our understanding. As a general rule, however, specific adsorption can be classified roughly into three groups:

(1) Very weak specific adsorption

It is probably safe to state that no ion is really one hundred percent indifferent. NaF on mercury approaches this condition. Alkali-ions on AgI and on most oxides are weakly specifically adsorbing. Often, the binding only takes place in pairs with surface charge groups (e.g. $\mathrm{Na^+}$–$\mathrm{I^-S}$ on AgI, where

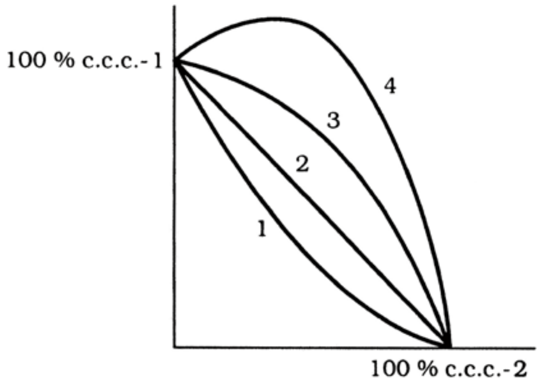

Figure 7-2. *Map of the possible trends for coagulation by salt mixtures. (1) Synergism, (2) additivity, (3) superadditivity, (4) antagonism. The axes gives the c.c.c.'s as fractions of the c.c.c.'s of the pure electrolyte.*

S stand for the groups on the surface of the solid). Insofar as such ions do not adsorb measurably on the uncharged surface, they cannot affect the p.z.c.; but when the surface charge is high, specificity shows up in the double layer capacitance and in the c.c.c. Overcharging does not occur.

(2) Moderate specific adsorption

Some alkali ions do adsorb on uncharged surface, and hence do shift the p.z.c. These ions do exhibit overcharging, at least over a short pH-range around the p.z.c. However, the effect is too minor to detect electrokinetically or by stability experiments.

Specific adsorption of this kind is more common for monovalent anions than for mono-valent alkali- or alkaline earth cations. This difference is probably mainly caused by their larger radius (and, hence polarizability), but even at the same ionic radius there are substantial differences between the enthalpies and entropies of hydration of cations and anions. A typical illustration is given by relative simple anions such as NO_3^- which can shift the p.z.c. of AgI; but it is difficult to stabilize AgI sols that are positively charged by adsorption of the charge-determining Ag^+ ions, because of strong co-adsorption of NO_3^- ions.

Moderate specific adsorption, as meant here, does lead to overcharging, but for solid surfaces its detectability via electrophoresis or stability studies is not easy because it is measurable only under conditions where the sols are unstable. The evidence essentially stems from double layer studies, including the shift of the p.z.c. with c_{salt} which takes place in the opposite direction as the i.e.p. that can be measured by streaming potentials.

(3) Strong specific adsorption

Multivalent ions, especially cations, form a class of their own, because overcharging has frequently been observed for them. The problem is that it is not the ion as such which causes the overcharging, but one, or more, hydrolyzed species. Complexes of these ions form in the solution and these can be very surface active. The composition of adsorbed complexes depends, however, on pH and quite often differs from that in solution. The identification of these surface complexes, and their relevance for the interpretation of the Schulze-Hardy type phenomena and overcharging, therefore requires much systematic research, first by studying the effect of pH on surface charge, ζ-potential, and stability. Although not so much comprehensive investigations are available now, partial studies suggest that the following conclusions could be drawn, upon which some of the trends may be sketched and shown in Figure 7-3.

3. At low pH, Th^{4+} and Al^{3+} -ions do not form complexes in the solution or in the double layer. They coagulate AgI sols with very low c.c.c. but cannot overcharge.
4. At high pH, depending on the nature of the metal ion, complexes are formed. Now overcharging is observed at sufficiently high c_{salt}, and sols are restabilized, having become positively charged. Eventually, a second c.c.c. is attained, but now with NO^-_3 as the counterion. In this manner, irregular series develop in the coagulation behaviour.
5. For bivalent metal ions, overcharging is observed if they are hydrolysable and the pH is not too low.
6. There are indications that, at very high pH, the adsorbability of the hydroxy-complexes decreases, eventually to disappear completely.

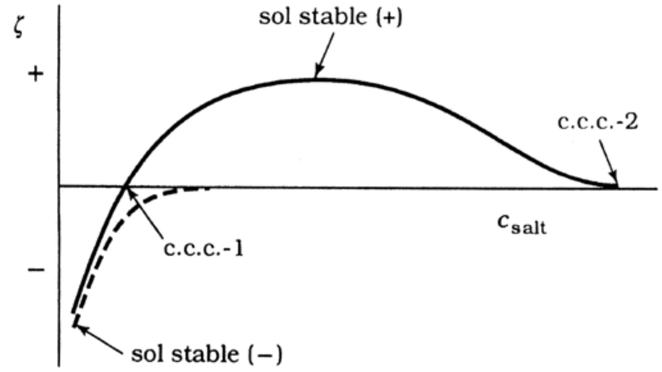

Figure 7-3. *Sketch of the stability regions for AgI sols in the presence of hydrolysable multivalent counterions. – high pH, – low pH. The values of ζ and the two c.c.c.'s depend on the nature and valency of the cation.*

8 Discussion and conclusions

There is a vast literature describing the behaviour of colloids in electrolyte solutions. In particular, several recent books have thoroughly compiled and described the forces and mechanisms involved. We have extracted and compiled much of this information in a systematic way we deem useful for us to develop models which are intended to describe the "chemical erosion" of colloidal smectite particles from bentonite clays into low ionic strength water. The specific aim is to assess the possible loss of the buffer surrounding canisters containing high level nuclear waste in the Swedish repository of KBS-3 type.

This report mainly concerns itself with the DLVO theory and its extensions. However, there have been a considerable number of papers which criticise various aspects of this theory and propose alternative approaches to improve on it. For example, the hypernetted chain approximations /32/ and the Monte Carlo simulations /33/ both suggest that under some circumstances highly charged particles with divalent counterions can develop strong but short-range attractive forces, by virtue of ion-ion correlations. Also, the Coulombic attraction theory has been proposed recently by Sogami and Ise /34, 35, 36/ to confirm the existence of a long-range attractive electrostatic force in colloidal suspensions. We have not included these and similar papers in the present report.

9 Notation and constants

Symbols

a	radius	m
c	concentration	molm^{-3}
c	velocity of light in a vacuum	ms^{-1}
d	thickness of the Stern layer	m
e	elementary charge	C
f_k	numbers of electrons oscillating with frequency	–
h	Plank constant	J s
h	separation between particles (planes) between Stern layers	m
k_B	Boltzmann constant	J K^{-1}
l	dipole length	m
m	electron mass	kg
n	vibrational quantum numbers	–
n^σ	number (excess) of moles in interface	mol
p, $\mathbf{p}$	dipole moment	C m
q	electric charge	C
r, $\mathbf{r}$	distance between dipole centres	m
s	distance between macrobodies	m
x	distance from surface or Helmholtz plane	m
x_j	mole fraction of ions of type j in the bulk solution	–
y	dimensionless potential	–
z	valence number	–
A	area	m^2
A	Hamaker constant	J
B	retarded Hamaker constant	J m
C	differential capacitance	C m^{-2} V^{-1}
E, $\mathbf{E}$	electric field strength	N C^{-1} or V m^{-1}
F	Faraday constant	C mol^{-1}
F_E	elliptic integral of the first kind	–
F^σ	interfacial (excess) Helmholtz energy	J
G	Gibbs energy	J
G^σ	interfacial (excess) Gibbs energy	J
G^σ_a	interfacial (excess) Gibbs energy per unit area	J m^{-2}
I	ionic strength	mol m^{-3}
K	integral capacitance	C m^{-2} V^{-1}
K_j	intrinsic binding constant	–
K_a	acid dissociation constant	–
K_b	base dissociation constant	–
K_w	water dissociation constant	–
K_{str}	solvent structure-mediated interaction constant	N m^{-2}
R	gas constant	J K^{-1} mol^{-1}
S	entropy	J K^{-1}
T	absolute temperature	K
V_w	molar volume of water	m^3 mol^{-1}

Greeks

α	polarizability	$C\ V^{-1}\ m^2$ or $C^2\ J^{-1}\ m^2$
β	interaction parameter of Van der Waals interaction	$J\ m^{-6}$
δ	acid-base dissociation coefficient	–
ε	relative dielectric permittivity	–
ε_0	dielectric permittivity of vacuum	$C^2\ N^{-1}\ m^{-2}$ or $C\ m^{-1}\ V^{-1}$
φ	abbreviation, given by $\varphi = (8\varepsilon_0\varepsilon cRT)^{-1/2}$	$m^2\ C^{-1}$
γ	surface tension	$N\ m^{-1}$
κ	reciprocal Debye length	m^{-1}
μ	chemical potential	$J\ mol^{-1}$
v	frequency	s^{-1}
ω	angular frequency	s^{-1}
ρ	space charge density	$C\ m^{-3}$
ρ_w	water density	$kg\ m^{-3}$
ρ_N	number density	m^{-3}
σ^0	surface charge density	$C\ m^{-2}$
σ^d	diffuse charge density	$C\ m^{-2}$
τ	characteristic time	s
ξ	macroscopic vibration frequency	s^{-1}
ψ	allowed energy of harmonic oscillators, Schrödinger equation	J
ψ	potential	J
ψ^0	surface potential	V
ψ^d	diffuse potential	V
ζ	electrokinetic potential	V
Φ	potential energy between two molecules	J
Γ	surface (excess) concentration	$mol\ m^{-2}$
Π	disjoining pressure	$N\ m^{-2}$
Ω	solid angle	–

Constants

h	Plank constant	$6.6260689633\times10^{-34}$ J s
k_B	Boltzmann constant,	$1.380\ 650424\times10^{-23}\ J\ K^{-1}$
ε_0	dielectric permittivity of vacuum	$8.8541878176\times10^{-12}\ C^2\ N^{-1}\ m^{-2}$
R	gas constant	$8.314472\ J\ K^{-1}\ mol^{-1}$
F	Faraday constant	$96\ 485.3383\ C\ mol^{-1}$

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