3. Theory

Crystallization is a separation and purification technique employed to produce a wide variety of materials. Crystallization may be defined as a phase change in which a crystalline product is obtained from a solution. A solution is a mixture of two or more species that form a homogenous single phase. Solutions are normally thought of in terms of liquids, however, solutions may include solids suspension. Typically, the term solution has come to mean a liquid solution consisting a solvent, which is a liquid, and a solute, which is a solid, at the conditions of interest. The solution to be ready for crystallization must be supersaturated. A solution in which the solute concentration exceeds the equilibrium (saturated) solute concentration at a given temperature is known as a supersaturated solution [66]. There are four main methods to generate supersaturation that are the following:

- Temperature change (mainly cooling),
- Evaporation of solvent,
- Chemical reaction, and
- Changing the solvent composition (e.g. salting out).

The Ostwald-Miers diagram shown in Fig. 3.1. illustrates the basis of all methods of solution growth. The solid line represents a section of the curve for the solute / solvent system. The upper dashed line is referred to as the super-solubility line and denotes the temperatures and concentration where spontaneous nucleation occurs [67]. The diagram can be evaluated on the basis of three zones:

- The stable (unsaturated) zone where crystallization is impossible,
- The metastable (supersaturated) zone where spontaneous nucleation is improbable but a crystal located in this zone will grow and
- The unstable or labile (supersaturated) zone where spontaneous nucleation is probable and so the growth.

Crystallization from solution can be thought of as a two step process. The first step is the phase separation, (or birth), of a new crystals. The second is the growth of these crystals to larger size. These two processes are known as nucleation and crystal growth, respectively. Analysis of industrial crystallization processes requires knowledge of both nucleation and crystal growth.
The birth of a new crystals, which is called nucleation, refers to the beginning of the phase separation process. The solute molecules have formed the smallest sized particles possible under the conditions present. The next stage of the crystallization process is for these nuclei to grow larger by the addition of solute molecules from the supersaturated solution. This part of the crystallization process is known as crystal growth. Crystal growth, along with nucleation, controls the final particle size distribution obtained in the system. In addition, the conditions and rate of crystal growth have a significant impact on the product purity and the crystal habit. An understanding of the crystal growth theory and experimental techniques for examining crystal growth from solution are important and very useful in the development of industrial crystallization processes. The many proposed mechanisms of crystal growth may broadly be discussed under a few general headings [67-70]:

- Surface energy theories
- Adsorption layer theories
- Kinematic theories
- Diffusion - reaction theories
- Birth and spread models

![Figure 3.1: Ostwald-Miers diagram for a solute/solvent system [67].](image)

3.1. The Three-Step-model

Modelling of crystal growth in solution crystallization is often done by the Two-Step-Model. The Two-Step-model describes the crystal growth as a superposition of two resistances: bulk diffusion through the mass transfer boundary layer, i.e. diffusion step,
and incorporation of growth units into the crystal lattice, i.e. integration step [67, 68].

The overall growth rate is expressed as:

\[ R_G = k_d (C_b - C_i) \]  
(diffusion step), \hspace{1cm} (3.1)

\[ R_G = k_r (C_i - C^*)' \]  
(integration step), \hspace{1cm} (3.2)

\[ R_G = k_G (C_b - C^*)^\varepsilon \]  
(overall growth), \hspace{1cm} (3.3)

where \((C_b - C^*)\) is the supersaturation.

The Two-Step-Model is totally ignoring the effect of heat transfer on the crystal growth kinetics. In the literature there is little evidence for the effects of heat transfer on the crystal growth kinetics in the case of crystallization from solution. Matsuoka and Garside [3] give an approach describing the combined heat and mass transfer in crystal growth processes. The so called Three-Step-model of combined mass and heat transfer takes the above mentioned effects into account [1-3]. A mass transfer coefficient is defined which includes a dimensionless temperature increment at the phase boundary constituted by the temperature effect of the liberated crystallization heat and the convective heat transfer. For simplicity the transport processes occurring during growth will be described in terms of the simple film theory. This has the advantage that the resulting equations can be easily solved and the predictions do not differ significantly from those derived using the boundary layer theory [71, 72]. Conditions in the fluid adjacent to the growing crystal surface are illustrated in Fig. 3.1.1. The mass transfer step can be presented by the equation:

\[ R_G = k_d (C_b - C_i) = k_d [(C_b - C^*_b) - (C_i - C^*_i) - (C^*_i - C^*_b)] \]

\[ = k_d [\Delta C_b - \Delta C_i - (T_i - T_b) \frac{dC^*}{dT}] \]  
(3.4)

where \(C^*_i\) and \(C^*_b\) are the saturation concentrations evaluated at the interface and bulk temperatures, respectively. The effect of bulk flow, important at high mass fluxes, is neglected in Eq. 3.4. It is also assumed that the temperature difference \((T_i - T_b)\) is sufficiently small for the solubility curve to be assumed linear over this temperature range. A heat balance relating heat evolution to convective transfer gives:
Theory

\[ R_G = \frac{h(T_i - T_b)}{-\Delta H} \] (heat transfer),

(3.5)

Combination of Eqs. 3.4 and 3.5 gives

\[ R_G = \frac{k_d}{1 + \frac{-\Delta H \times k_d}{h} \cdot \frac{dC^*}{dT}} = \left( \Delta C_b - \Delta C_i \right) = k_d \left( \Delta C_b - \Delta C_i \right) \]

(3.6)

\[ \beta_d = \frac{-\Delta H \times k_d}{h} \cdot \frac{dC^*}{dT} \]

(3.7)

Where \( \beta_d \) is defined by Matsuoka and Garside [3] as a dimensionless number for the temperature increase at the crystal surface and therefore as measure of the heat effect on growth kinetics.

![Diagram showing concentration and temperature profiles to the crystal surface](image)

**Figure 3.1.1.:** Concentration and temperature profiles to the crystal surface as assumed in the simple film theory [1].

The analogy between mass transfer and heat transfer is given by [73]:

\[ \frac{h}{k_d} = \rho_c cp \left( \frac{Sc}{Pr} \right)^{2/3} = \rho_c cp Le^{2/3} \]

(3.8)

substitution Eq. 3.8 into Eq. 3.7 gives the following equation:

\[ \beta_d = \frac{-\Delta H}{\rho_c cp Le^{2/3}} \cdot \frac{dC^*}{dT} \]

(3.9)
The general expression for the overall growth rate can be obtained by combining Eqs. 3.1, 3.2 and 3.6:

\[ R_G = k_r \left[ (C_b - C^*) - R_G \frac{1 + \beta_d}{k_d} \right]^r \]  \hspace{1cm} (3.10)

Matsuoka and Garside [3] give a limit \( \beta_d \) must be \( > 10^{-2} \), for values below which the influence of the heat transfer on the crystal growth kinetics can be neglected.

The dissolution process is, on the contrary, quite frequently described only by use of the diffusion step. What is not true since there is definitely a surface disintegration step [4, 5]. In other words dissolution is the 100% opposite of crystal growth. However, a justification for the model assumption that dissolution can be seen as just diffusion controlled is due to experimental results which show a linear dependence on the concentration difference (undersaturation). Furthermore, the dissolution process is happening according to literature much faster (4 to 6 times) than the crystal growth process so that a possible surface reaction resistance is here difficult to observe [4, 5]. The assumption that the dissolution of crystals involves the sole diffusion step is therefore, in many case valid:

\[ R_D = k_d (C^* - C_b) \]  \hspace{1cm} (3.11)

Two methods, the differential and integration method, are mainly used for the measurements of the growth rates in fluidized bed experiments [74]. In this study the differential method was used. In the differential method, the crystallization is seeded by adding a few grams of crystals with a known sieve aperture into a supersaturated solution. The seed crystals grow in the supersaturated solution. Since the amount of crystals is small, it is assumed that the concentration of the solution does not change during the growth. The other assumptions are as follows:

- The number of seed crystals put into the crystallizer is equal to the number of crystals taken out from the crystallizer.
- There is no crystal loss, an assumption which is always valid for an experienced experiment.
- The shape factor of the growing crystals are considered to be the same. This assumption is not always true especially in the case of surface nucleation. In this case, growth values are thought of as average values.
If the amount of the crystals put into the crystallizer is $M_1$ and the amount of the crystals taken out from the crystallizer is $M_2$, they can be related to the size of the crystals $L$ as shown in the following equations [75]:

$$M_1 = \alpha \rho L_1^3,$$  (3.12)

$$M_2 = \alpha \rho L_2^3,$$  (3.13)

where $L_1$ and $L_2$ are the characteristic size of the crystals input and the output, respectively. The overall linear growth rate $G$ (m/s) is defined as the rate of change of characteristic size:

$$G = \frac{\Delta L}{t}$$  (3.14)

The expression for the growth rate in terms of size of the seed crystals and the weight of the crystals can be given by:

$$G = \frac{L_1}{t} \left[ \left( \frac{M_2}{M_1} \right)^{\frac{1}{3}} - 1 \right]$$  (3.15)

$G$ and $R_G$ are related to each other as follows:

$$R_G = \frac{3\alpha_i}{\beta_i} \rho_c G$$  (3.16)

where $\beta_i$ and $\alpha_i$ are surface and volume shape factors, respectively. $M_1$ and $M_2$ are experimentally obtained. The growth rate, $R_G$, and the dissolution rate, $R_D$, are calculated from Eq. 3.16 by knowing $L_1$ and $t$.

### 3.2. The concept of effectiveness factors

When crystals grow the rate at which solute is deposited in the crystal lattice is controlled by two resistances in series, those offered by diffusion through the boundary layer and by reaction at the crystal surface. If the rate equations for these two steps are known, the overall crystal growth rate can be easily calculated. It is much more difficult to deduce the kinetics of the individual resistances from measured overall growth rates. Therefore, a quantitative measure of the degree of diffusion or surface integration control may be made through the concept of effectiveness factors. A crystal growth rate effectiveness factors, $\eta$, is defined by Garside [76] as the ratio of the overall growth rate to the growth rate that would be obtained if diffusion offered negligible resistance is given by:
\[ \eta_r = (1 - \eta_r D_a)^{\gamma} \]  

(3.17)

where \( \eta_r \) is the integration effectiveness factor and \( D_a \) is the Damköhler number for crystal growth which represents the ratio of the pseudo first order rate coefficient at the bulk conditions to the mass transfer coefficient, defined by:

\[ D_a = \frac{k_r}{k_d} \left( C_b - C^* \right)^{\gamma-1} \]  

(3.18)

It will also be convenient to define a diffusion effectiveness factor, \( \eta_d \) as:

\[ \eta_d = D_a (1 - \eta_d)^{\gamma} \]  

(3.19)

The heat of crystallization produced at the crystal surface will change the solution temperature at this point and hence alter the rates of the kinetics processes. Consequently the effectiveness factor will change from that evaluated under bulk conditions. The non-isothermal effectiveness factor, \( \eta' \), is defined as the ratio of actual growth rate to the rate that would be obtained if the bulk liquid conditions assumed to exist at the crystal surface:

\[ \eta' = \frac{\text{growth rate at } \Delta C_i \text{ and } T_i \text{ (i.e. interface conditions)}}{\text{growth rate at } \Delta C_b \text{ and } T_b \text{ (i.e. bulk conditions)}} \]  

(3.20)

an analysis similar to that of Carberry and Kulkrani [72] for chemical reaction can be applied to the crystal growth case to yeild

\[ \eta' = D_a (1 - \eta')^{\gamma} \exp \left[ -\varepsilon_0 \left( \frac{1}{1 + \eta' D_a B (1 + \beta_d)^{\gamma-1}} - 1 \right) \right] \]  

(3.21)

where the Damköhler number crystal growth, \( D_a \), is defined by

\[ D_a = \frac{k_r b}{k_d} \left( \Delta C_b \right)^{\gamma-1} \]  

(3.22)

and represent the ratio of the pseudo-first order rate coefficient at the bulk conditions to the mass transfer coefficient. The Arrhenius number is defined by:

\[ \varepsilon_0 = \frac{E}{R T_b} \]  

(3.23)

and
\[ \beta = \frac{-\Delta H}{\rho_c c_p L e^{2/3}} \frac{\Delta C_b}{T_b} \]  

(3.24)

is the ratio of the interface adiabatic temperature rise to the bulk temperature. When \( \beta_d \ll 1 \), Eq. 3.21 becomes identical to that given by Carberry and Kulkrani [72], i.e.:

\[ \eta' = Da (1-\eta')' \exp \left[ -e_0 \left( \frac{1}{1 + \eta' D_a \beta} - 1 \right) \right] \]

(3.25)

### 3.3. Model for crystal growth in the presence of impurities

It is well known that the influence of impurities on the crystal form and the growth rate is based on the adsorption of the foreign molecules on the surface. The change of crystal form is based on a difference in adsorption energies on different crystal faces. Foreign molecules will be adsorbed preferentially on surfaces where the free adsorption energy has its maximum. Surface adsorbed impurities can reduce the growth rate of crystals by reducing or hindering the movement of growth steps. Depending on the amount and strength of adsorption, the effect on crystal growth can be very strong or hardly noticeable.

The step advancement velocity is assumed [49] to be hindered by impurity species adsorbing on the step lines at kink sites by a modified mechanism, the original version of which was proposed by Cabrera and Vermilyea [14]. Step displacement is pinned (or stopped) by impurities at the points of their adsorption and the step is forced to curve as shown schematically in Fig. 3.3.1.

The advancement velocity of a curved step, \( v_r \), decreases as the radius of curvature, \( \rho \), is reduced and it becomes zero just at a critical size, \( r = r_c \). It is given simply by the following equation [78], if the relative supersaturation is small (\( \sigma \ll 1 \)):

\[ \frac{v_r}{v_0} = 1 - \frac{r_c}{r} \]

(3.26)

where \( v_0 \) is the velocity of linear step and \( r_c \) is the critical radius of a two-dimensional nucleus. At \( r \leq r_c \) the step cannot move. The instantaneous step advancement velocity changes with time during the step squeezes out between the adjacent adsorbed impurities because the curvature changes with time. The maximum velocity is \( v_0 \) (of a linear step)
and the minimum instantaneous step velocity $v_{\text{min}}$ is given at a curvature of $r = l/2$ ($l$ is average spacing between the adjacent adsorbed impurities) by:

$$v_{\text{min}} = \frac{v_0}{1 - \frac{r_c}{l/2}}.$$  \hfill (3.27)

Time-averaged advancement velocity $v$ of a step is approximated by the arithmetic mean of $v_0$ and $v_{\text{min}}$ [77] as:

$$v = \frac{v_0 + v_{\text{min}}}{2}.$$  \hfill (3.28)

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{impurity_adsorption.png}
\caption{Model of impurity adsorption. Impurity species are assumed to be adsorbed on the step lines at kink sites and to retard the advancement of the steps [77].}
\end{figure}

Combining Eqs. 3.27 and 3.28 one obtains the following equation for the average step advancement velocity as a function of the average spacing between the impurities, $l$:

$$\frac{v}{v_0} = 1 - \frac{r_c}{l}.$$  \hfill (3.29)

while $v = 0$ for $l \leq r_c$.

This simple equation was thus obtained by assuming the linear array of sites on the step lines and by using the arithmetic mean of the maximum and minimum step velocities as an average step velocity.
The coverage of active sites by impurities $\theta$ can be related to the average distance between the active sites $\lambda$, from a simple geometric consideration, under the assumption of linear adsorption on the step lines (linear array) as:

$$\theta = \frac{\lambda}{l} \quad (3.30)$$

on the other hand, the critical radius of a two-dimensional nucleus is given by Burton et al. [78] as:

$$r_c = \left( \frac{\gamma a}{k_B T\sigma} \right) \quad (for \, \sigma \ll 1) \quad (3.31)$$

Insertion of Eqs. 3.30 and 3.31 into Eq. 3.29 gives the following equation:

$$\frac{v}{v_0} = 1 - \left\{ \frac{\gamma a}{k_B T\sigma \lambda} \right\} \theta \quad (3.32)$$

where $\gamma$ is the linear edge free energy of the step, $a$ is the size of the growth unit (area per growth unit appearing on the crystal surface), $k_B$ is the Boltzmann constant, $T$ is the temperature in Kelvin.

As soon as kinks and steps are occupied by foreign molecules, the coverage of crystal faces causes a reduction in growth rate [48]. If all active centres for growth are blocked, growth rates can be reduced to zero. Kubota et al. [77], introduce the impurity effectiveness factor, $\alpha$. The effectiveness factor $\alpha$ is a parameter accounting for the effectiveness of an impurity under a given growth condition (temperature and supersaturation). Thus, the step advancement velocity can be written as a function of temperature and supersaturation:

$$\alpha = \left( \frac{\gamma a}{k_B T\sigma \lambda} \right) \quad (3.33)$$

Eq. 3.32 can be changed to

$$\frac{v}{v_0} = 1 - \alpha \theta \quad (for \, \alpha \theta < 1) \quad (3.34)$$

where $v = 0$ for $\alpha \theta \geq 1$.

This impurity effectiveness factor can be less than or equal or greater than one. $\alpha$ decreases with increasing supersaturation and is independent of $K$. In Fig. 3.3.2., the
relative step velocities, calculated from Eq. 3.34, are shown for different effectiveness factors, $\alpha$, as a function of the dimensionless impurity concentration $K_{c_{imp}}$.

**Figure 3.3.2.:** Theoretical relationship between the relative mass growth rate, $R_G/R_{G_0}$, and the dimensionless impurity concentration, $K_c$, for different value of $\alpha$. (Diagram based on the work of [77]).

It is clear from Fig. 3.3.2. that, when $\alpha > 1$, the relative velocity decreases very steeply with increasing impurity concentration and reaches zero at a small value of $K_{c_{imp}}$. For $\alpha = 1$, a full coverage of the crystal surface leads to step velocity equal to zero. For $\alpha < 1$, however, the step velocity never approaches zero but approaches a non-zero value as $K_{c_{imp}}$ is increased. This value is increasing with smaller $\alpha$ and is one at a value of $\alpha = 0$.

If an equilibrium adsorption is assumed for an impurity [49, 77], the surface coverage $\theta$ in Eq. 3.36 is replaced by an equilibrium value $\theta_{eq}$:

$$\frac{\nu}{\nu_0} = 1 - \alpha \theta_{eq}$$  \hspace{1cm} (3.35)

and the step advancement velocity may be related to the concentration of the impurity $c_{imp}$ if an appropriate isotherm is employed. Although any adsorption isotherm can be used for this purpose. Therefore, the coverage, $\theta_{eq}$, of adsorption sites may be described by the usual adsorption isotherms [35, 79, 80]:
In this equation $K$ is constant. The constant $K$ of Eq. 3.36 is given by [79, 80]:

$$K = \exp\left(\frac{Q_{\text{diff}}}{RT}\right)$$

(3.37)

where $Q_{\text{diff}}$ is the differential heat of adsorption corresponding to $\theta_{eq}$.

In the case of a spiral growth mechanism, the relationship between the step velocity at a crystal face, $v$, and the fraction coverage, $\theta_{eq}$, of the surface may be given by [81, 82]:

$$(v - v/v_0)^n = \alpha^n \theta_{eq}$$

(3.38)

The exponent $n=1$ and 2 represents the case at which impurity adsorption occurs at kinks in step edges and on the surface terrace, respectively.

The relative step velocity in Eq. 3.38, can be replaced by the relative growth rate $R_G/R_{Go}$ if the growth rate is assumed to be proportional to the step velocity:

$$(R_{Go} - R_G / R_{Go})^n = \alpha^n \theta_{eq}$$

(3.39)

The previous model of impurity adsorption considering kinks and the surface terraces deal with the kinetic aspect of adsorption of impurities of F faces, neglecting the thermodynamic effects. Therefore, for all the above equations it is true that growth rates are reduced, when impurities are present in the solution. Generally, experiments carried out in a fluidized bed crystallizers [83-86] showed that the addition of small amounts of impurities lead to a decrease in growth rates. This is in good agreement with theoretical predictions published in the literature [84, 87].

### 3.4. Electrical double layer

The charge that develops at the interface between a particle surface and its liquid medium may arise by any of several mechanisms. Among these are the dissociation of inorganic groups in the particle surface and the differential adsorption of solution ions in
to the surface region. The net charge at the particle surface affects the ion distribution in the nearby region, increasing the concentration of counter-ions close to the surface. Thus, an electrical double layer is formed in the region of the particle-liquid interface [88-90]. The electric double layer plays a major role in diverse area such as adhesion, self-assembly, filtration, wetting, electrokinetics, and it is perhaps the major determinant the colloidal interactions and colloid stability.

If a liquid moves tangential to a charged surface, then so called electrickinetic phenomena. Electrickinetic phenomena can be divided into four categories [88-90]:

- **Electrophoresis**: the movement of charged particles suspended in a liquid under the influence of an applied electric field.
- **Electroosmosis**: the movement of liquid in contact with a stationary charged solid, again in response to an applied electric field.
- **Streaming Potential**: is generated when a liquid is forced under pressure to move in contact with a stationary charged solid.
- **Sedimentation Potential**: may be regarded as the converse of electrophoresis. It arises when charged particles move through a stationary liquid under the influence of gravity.

In all these phenomena the zeta (ζ) potential plays a crucial role.

**What is zeta (ζ) potential ?**

Most particles in a polar medium such as water posses a surface charge. A charged particle will attract ions of the opposite charge in the dispersant, forming a strongly bound layer close to the surface of the particle. These ions further away from the core particle make up a diffuse layer, more loosely bound to the particle. Within this diffuse layer is a notional boundary, inside which the particle and its associated ions act as a single entity, diffusing through the dispersion together. The plane at this boundary is known as the surface of shear, or the slipping plane [88].

**Surface of shear** is an imaginary surface which considered to lye to the solid surface and within which the fluid is stationary. In the case of a particle undergoing electrophoresis, the surface forms a sheath which envelopes the particle. All of the material inside that sheath forms the kinetic unit. So that the particle moves along with a certain quantity of the surrounding liquid and its contained charge. Measurement of
electrophoretic mobility (i.e. the velocity per unit electric field) therefore gives a measure of the net charge on the solid particle. The analysis of the forces on the solid or the liquid can be carried out in terms of either charge or electrostatic potential. In the later case one calculates the average potential in the surface of shear; this is called the \( \zeta \)-potential [88].

**Why not use the surface charge?**

The interaction of particles in a polar liquid is not governed by the electrical potential at the surface of the particle, but by the potential that exists at the slipping plane (surface of shear). The \( \zeta \)-potential and surface charge can be entirely unrelated, so measurement of surface charge is not an useful indication of particle interaction. Therefore, to utilize electrostatic control, it is the \( \zeta \)-potential of a particle that is needed to know rather than its surface charge.

### 3.4.1. Origins of surface charge

Most particles acquire a surface electric charge when brought into contact with a polar (e.g. aqueous) medium. The more important mechanisms which caused to acquire the particle a charge are [88]:

- Ion dissolution, and
- Ionization of surface groups.

As a result:

- Ions of opposite charge (counter–ions) are attracted towards the surface.
- Ions of the same charge (co–ions) are repelled away from the surface.

The above mentioned leads to the formation of an electric double layer made up of the charged surface and a neutralising excess of counter-ions over co-ions distribution in a diffuse manner in the aqueous solution.
3.4.1.1. Ion dissolution

This is defined as acquiring a surface charge by unequal dissolution of the oppositely charged ions of which they are composed. For the AgI/water system, for instance, the charge separation at the interface between the crystal and an aqueous electrolyte solution can be thought of as being due to either the differential of adsorption of ions from an electrolyte solution on to a solid surface, or the differential solution of one type of ion over the other from a crystal lattice. The surface of the crystal may be treated as a separate phase and, at equilibrium, the electrochemical potential of both $Ag^+$ and $I^-$ ions must be the same in this phase as they are in the bulk aqueous solution:

$$\mu_0^s (Ag^+) + k_B T \ln [a_s (Ag^+)] + zq \Phi_s = \mu_0^l (Ag^+) + k_B T \ln [a_l (Ag^+)] + zq \Phi_l$$ (3.40)

$\mu_0^s (Ag^+)$ and $\mu_0^l (Ag^+)$ are the chemical standard potential at the crystal surface and in solution, respectively. $\Phi_s$ and $\Phi_l$ are the Galvani potential in the crystal and in the solution. In particular, the equation is valid at the point of zero charge (the concentration of the potential-determined ion at which the colloid has no net charge is called the point of zero charge, pzc) [88, 92]:

$$\mu_0^l (Ag^+) + k_B T \ln [a_{pzc} (Ag^+)] = \mu_0^s (Ag^+) + k_B T \ln [a_{pzc} (Ag^+)] + zq \Delta \chi_{pzc}$$ (3.41)

$\Delta \chi_{pzc}$ is the difference of the Galvani potentials, which is caused solely by dipoles in the interface, not by free charges. The subtract Eqs. 3.40 and 3.41 lead to:

$$k_B T \ln \frac{a_{l} (Ag^+)}{a_{pzc} (Ag^+)} = zq (\Phi_s - \Phi_l - \Delta \chi_{pzc})$$ (3.42)

It is assumed that $a_s (Ag^+) = a_{pzc} (Ag^+)$. The expression in brackets is called surface potential, $\psi_0$. Thus one obtains the Nernst equation:

$$\psi_0 = \frac{k_B T}{zq} \ln \frac{a_s (Ag^+)}{a_{pzc} (Ag^+)}$$ (3.43)

The concentration of $Ag^+$ (and thus that of $I^-$) determines the surface potential. During the derivation it is assumed that $a_s (Ag^+) = a_{pzc} (Ag^+)$. That means that during the
charging of the AgI surface the activity of the Ag\(^+\) ions on the surface do not change. This assumption is justified to a large extent, because the number of Ag\(^+\) ions on the surface changes only slightly. The relative number of ions, i.e. the number of the additionally adsorbed ions upon a variation of the potential, is very small.

### 3.4.1.2. Ionization of surface groups

The ionization of surface groups, i.e. charge development, is commonly observed with carboxylic acid, amine and oxide surface faces. In these systems the charge development (and its sign) depends on the pH of the solution. The potential determining ions are OH\(^-\) and H\(_3\)O\(^+\). Oxide surfaces, for example, are considered to posses a large number of amphoteric hydroxyl groups which can undergo reaction with either H\(_3\)O\(^+\) or OH\(^-\) depending on the pH [88, 90-94]:

\[
\begin{align*}
\text{MOH} + H_3O^+ & \leftrightarrow MOH^+ + H_2O \\
\text{MOH} + OH^- & \leftrightarrow MO^- + H_2O
\end{align*}
\]

This shows the amphoteric nature of the surface. At high pH the surface is negatively charged, and low pH it is positively charged. The surface potential, \(\Psi_0\), is given by the Nernst equation as a function of H\(_3\)O\(^+\)/OH\(^-\) ions:

\[
\Psi_0 = -2.303 \frac{k_BT}{q} (pH - pH_{pzc})
\]

is no longer satisfactory for describing the surface potential because the assumption that \(a_s(H_3O^+) = a_s^{pzc}(H_3O^+)\) is clearly untenable. In these systems there are very few H\(_3\)O\(^+\) ions present on the surface at the \(pzc\) and it is certainly not true that the number of additional H\(_3\)O\(^+\) ions required to establish the charge is insignificant by comparison. A modified Nernst equation was derived by Smith [97]. Essentially Eq. 3.45 must be replaced by:

\[
\Psi_0 = -2.303 \frac{k_BT}{q} \left[ pH - pH_{pzc} + \log \frac{a_s(H^+)}{a_s^{pzc}(H^+)} \right]
\]

The additional term has the effect of lowering the expected double layer potential which is in keeping with the experimental observation.
3.4.2. Electrophoresis

Electrophoresis is defined as the migration of ions under the influence of an electric field. The force \((F = qE)\) imparted by the electrical field is proportional to its effective charge, \(q\), and the electric field strength, \(E\). The translation movement of the ion is opposed by a retarding frictional force \((F_f = fv)\), which is proportional to the velocity of the ion, \(v\), and the friction coefficient, \(f\). The ion almost instantly reaches a steady state velocity where the acceleration force equals the frictional force.

\[ qE = f v \quad \Rightarrow \quad v = \frac{q}{f} E = u E \]  \( (3.47) \)

Here \(u\) is the electrophoretic mobility of the ion, which is a constant of proportionality between the velocity of the ion and the electric field strength. The electrophoretic mobility is proportional to the charge of the ion and inversely proportional to the friction coefficient. The friction coefficient of the moving ion is related to the hydrodynamic radius, \(a_1\), of the ion and the viscosity, \(\mu\), of the surrounding medium, \(f = 6\pi\mu a_1\), because \(u = q/f\), a larger hydrodynamic radius translates to a lower electrophoretic mobility.

The effective charge arises from both the actual surface charge and also the charge in the double layer. The thickness of the double layer is quantified by \(a_1\) parameter with the dimensions of inverse length \(k\), so that the dimensionless number \(ka_1\) effectively measures the ratio of particle radius to double layer thickness. The figure below illustrates the typical situation.

\[ \text{Figure 3.4.1.: Apparent charge distribution around a spherical particle at low potential [88].} \]
It turns out that $q$ can be estimated using some approximations. Providing that the value of charge is low, (zeta potential less than 30 mV or so) the Henry equation can be applied [88, 98-100]:

$$u = (2\varepsilon \zeta / 3\mu) f(ka_1)$$  \hspace{1cm} (3.48)

Henry's function, $f(ka_1)$, varies smoothly from 1 to 1.5 as $ka$ varies from 0 to $\infty$, these corresponding to limiting cases where the particle is much smaller than the double layer thickness, or much larger.

### 3.4.3. The diffusion double layer (The Gouy–Chapman model)

Surface charge cause an electrical field. This electrical field attracts counter ions. The layer of surface charges and counter ions is called electrical double layer. The first theory for the description of electrical double layers comes from Helmholtz started with the fact that a layer of counter ions binds to the surface charges [88-96]. The counter ions are directly adsorbed to the surface. The charge of the counter ions exactly compensates the surface charge. The electrical field generated by the surface charge is accordingly limited to the thickness of a molecular layer. Helmholtz could interpret measurements of the capacity of double layers; electrokinetic experiments, however, contradicted his theory.

Gouy and Chapman went a step further. They considered a possible thermal motion of the counter ions. This thermal motion leads to the formation of a diffuse layer, which is more extended than a molecular layer [88]. For the one-dimensional case of a planar, negatively charged plane this is shown in the illustration. Gouy and Chapman applied their theory on the electrical double layer of planar surface. Later, Debye and Hückel calculated the behaviour around spherical solids.

**Fig. 3.4.2.** portrays schematically the discrete regions into which the inner part of the double layer has been divided. First there is the layer of dehydrated ions (i.e. *Inner Helmholtz Plane, I.H.P.* ) having potential, $\Psi_0$, and surface charge, $\sigma_0$, and second there is the first layer of hydrated ions (i.e. *Outer Helmholtz Plane, O.H.P.*) having potential, $\Psi_d$, and charge, $\sigma_d$. The *O.H.P.* marks beginnings of the diffuse layer [88, 92].
The aim is to calculate the electrical potential, $\Psi$, near charged interfaces. Therefore, here a plane is considered with a homogenous distributed electrical charge density, $\rho$, which is in contact with a liquid. Generally charge density and potential are related by the Poisson equation [88-90]:

$$\nabla^2 \Psi = \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} = -\frac{\rho e}{\varepsilon \varepsilon_0}$$  \hspace{1cm} (3.49)

With the Poisson equation the potential distribution can be calculated once the position of all charges are known. The complication in our case is that the ions in solution are free to move. Since their distributions, and thus the charge distribution in the liquid, is unknown, the potential cannot be found only by applying the Poisson equation. Additional information is required.

This additional formula is the Boltzmann equation. If we have to bring an ion in solution from far away closer to the surface, electric work $W_i$ has to be done. The local ion density would be:

$$n_i = n_i^0 e^{-\frac{W_i}{k_B T}}$$  \hspace{1cm} (3.50)

$n_i^0$ is the density of the $i^{th}$ ion sort in the volume phase, given in particles/m$^3$. The local ion concentration depends on the electrical potential at the respective place. For example, if the potential at a certain place in the solution is positive, then at this place there will be more anions, while the cation concentration is reduced.
Now it is assumed that only electrical work has to be done. It is furthermore neglected for instance that the ion must displace other molecules. In addition, it is assumed that only a 1:1 salt is dissolved in the liquid. The electrical work required to bring a charged cation to a place with potential $\Psi$ is $W^+ = q\Psi$. For an anion it is $W^- = -q\Psi$. The local anion and cation concentration $n^-$ and $n^+$ are related with the local potential $\Psi$ through the Boltzmann factor:

$$n^- = n_0 e^{\frac{q\Psi}{k_B T}} \quad , \quad n^+ = n_0 e^{-\frac{q\Psi}{k_B T}}$$

(3.51)

$n_0$ is the volume concentration of the salt. The local charge density is:

$$\rho_c = q(n^- - n^+) = n_0 q \left( -\frac{q\Psi}{k_B T} - e^{\frac{q\Psi}{k_B T}} \right)$$

(3.52)

Substituting the charge density into Poisson’s equation gives the Poisson–Boltzmann equation:

$$\nabla^2 \Psi = \frac{n_0 q}{\varepsilon \varepsilon_0} \left( \frac{q\Psi(x,y,z)}{k_B T} - e^{\frac{q\Psi(x,y,z)}{k_B T}} - e^{\frac{q\Psi(x,y,z)}{k_B T}} \right)$$

(3.53)

This is a partial differential equation of second order. In most cases, it cannot be solved analytically. Nevertheless, some simple cases can be treated analytically.

**One dimensional geometry**

A simple case is the one-dimensional situation of a planar, infinitely extended plane. In this case the Poisson-Boltzmann equation only contains the coordinate vertical to the plane:

$$\frac{d^2 \Psi}{dx^2} = \frac{n_0 q}{\varepsilon \varepsilon_0} \left( \frac{q\Psi(x)}{k_B T} - e^{\frac{q\Psi(x)}{k_B T}} - e^{\frac{q\Psi(x)}{k_B T}} \right)$$

(3.54)

before it is solved this equation for the general case, it is illustrative to treat a special case:
A. **Low potential**

How does the potential change with distance for small surface potential? “Small” means, strictly speaking \( q |\Psi_0| \ll k_B T \). At room temperature that would be \( \approx 25 \) mV. Often the result is valid even for higher potentials, up to approximately 50-80 mV. With small potentials it can be expanded that the exponential functions into a series and neglect all but the first (i.e. the linear) term:

\[
\frac{d^2 \Psi}{dx^2} \approx \frac{n_0 q}{\varepsilon \varepsilon_0} \left( 1 + \frac{q \Psi}{k_B T} - 1 + \frac{q \Psi}{k_B T} \pm \ldots \right) = \frac{2n_0 q^2}{\varepsilon \varepsilon_0 k_B T} \Psi
\]

This is sometimes called the linearized Poisson-Boltzmann equation. The general solution of the linearized Poisson-Boltzmann equation is:

\[
\Psi(x) = C_1 e^{-kx} + C_2 e^{kx}
\]

with

\[
k = \sqrt{\frac{2n_0 q^2}{\varepsilon \varepsilon_0 k_B T}}
\]

\( C_1 \) and \( C_2 \) are constants which are defined by boundary conditions. For a simple double layer the boundary conditions are \( \Psi(x \to \infty) = 0 \) and \( \Psi(x = 0) = \Psi_0 \). The first boundary condition guarantees that with very large distances the potential disappears and does not grow infinitely. From this follows \( C_2 = 0 \). From the second boundary condition follows \( C_1 = \Psi_0 \). Hence, the potential is given by:

\[
\Psi = \Psi_0 e^{-kx}
\]

The potential decreases exponentially. The typical decay length is given by \( \lambda_D = k^{-1} \). It is called the Debye length.

The Debye length decreases with increasing salt concentration. That is intuitively clear: The more ions are in the solution, the more effective is the shielding of the surface charge. If one quantifies all the factors for water at room temperature, then for a monovalent salt with concentration \( c \) the Debye length is \( \lambda_D = 3/\sqrt{c} \) Å, with \( c \) in mol/l.
B. Arbitrary potential

Now comes the general solution of the one-dimensional Poisson-Boltzmann equation. It is convenient to treat the equation with dimensionless potential $y \equiv q\Psi/kT$.

The Poisson-Boltzmann equation becomes thereby:

$$\frac{d^2y}{dx^2} = \frac{n_0 q}{\varepsilon\varepsilon_0 k_B T} \left(e^y - e^{-y}\right) = \frac{2n_0 q^2}{\varepsilon\varepsilon_0 k_B T} \frac{1}{2} \left(e^y - e^{-y}\right) = k^2 \sinh y$$

(3.59)

To obtain this it is used:

$$\frac{d^2y}{dx^2} = \frac{q}{k_B T} \frac{d^2\Psi}{dx^2} \quad \text{and} \quad \sinh y = 1/2 \left(e^y - e^{-y}\right)$$

The solution of the differential equation 3.59 is:

$$\ln \left(\frac{e^{y/2} - 1}{e^{y/2} + 1}\right) = -kx + C$$

(3.60)

The potential must correspond to the surface potential for $x = 0$, that means $y(x = 0) = y_0$. With the boundary condition one gets the integration constant

$$\ln \left(\frac{e^{y_0/2} - 1}{e^{y_0/2} + 1}\right) = C$$

(3.61)

substitution results in

$$\ln \left(\frac{e^{y/2} - 1}{e^{y/2} + 1}\right) - \ln \left(\frac{e^{y_0/2} - 1}{e^{y_0/2} + 1}\right) = \ln \left(\frac{e^{y/2} - 1 + e^{y_0/2} + 1}{e^{y/2} + 1 + e^{y_0/2} - 1}\right) = -kx$$

(3.62)

$$\Rightarrow e^{-kx} = \frac{e^{y/2} - 1 + e^{y_0/2} + 1}{e^{y/2} + 1 + e^{y_0/2} - 1}$$

solving the Eq. 3.62 for $e^{y/2}$ leads to the alternative expression:

$$e^{y/2} = \frac{y_0/2 + 1 + e^{y_0/2} - 1)e^{-kx}}{e^{y_0/2} + 1 - (e^{y_0/2} - 1)e^{-kx}}$$

(3.63)

The potential and the ion concentrations are shown as an example in the illustration. A surface potential of 50 mV and a salt concentration (monovalent) of 0.1 M were assumed.
Figure 3.4.3.: The relation between the surface potential and salt concentrations.

It is clear that:

- The potential decreases approximately exponentially with increasing distance.
- The salt concentration of the counter ions decreases more rapidly than the potential.
- The total ion concentration close to the surface is increased.

In the following illustration the potential, which is calculated with the linearized form of the Poisson-Boltzmann equation (dashed), is compared with the potential which results from the complete expression. It can be seen that the decrease of the potential becomes steeper with increasing salt concentration. This reflects that the Debye length decreases with increasing salt concentration.

Figure 3.4.4.: The relation between the surface potential and electrical double layer thickness at different salt concentrations.
3.4.3.2. The Grahame equation

How are surface charge and surface potential related? This question is important, since the relation can be examined with the help of a capacity measurement. Theoretically this relation is described by the Grahame equation. One can deduce the equation easily from the so called electroneutrality condition. This condition demands that the total charge, i.e. the surface charge plus the charge of the ion in the whole double layer, must be zero.

The total charge in the double layer is \( \int_0^\infty \rho_e \, dx \) and it is leads to:

\[
\sigma = -\int_0^\infty \rho_e \, dx = \varepsilon_0 \int_0^\infty \frac{d^2 \Psi}{dx^2} \, dx = -\varepsilon_0 \frac{d\Psi}{dx} \bigg|_{x = 0} = 0 \tag{3.64}
\]

in the final step we has used \( \frac{d\Psi}{dx} \bigg|_{x = \infty} = 0 \). With

\[
\frac{dy}{dx} = \frac{d(q \Psi/k_B T)}{dx} = \frac{q}{k_B T} \frac{d\Psi}{dx} \quad \text{and} \quad \frac{dy}{dx} = -2k \, \sinh \frac{y}{2} \quad \text{follows}
\]

\[
\sigma = \sqrt{8 \, n_0 \, \varepsilon_0 \, k_B T} \, \sinh \left( \frac{q \Psi_0}{2k_BT} \right) \tag{3.65}
\]

For small potential one can expand \( \sinh x \) into a series \( (\sinh x = x + x^3/3! + \ldots) \) and break off after the first term. That leads to the simple relation:

\[
\sigma = \frac{\varepsilon_0 \Psi_0}{\lambda_D} \tag{3.66}
\]

The following illustration shows the calculated relation between surface tension and surface charge for different concentrations of a monovalent salt.

---

**Figure 3.4.5.** The relation between the surface potential and surface charge density at different salt concentrations.
It is clear that:

- For small potential $\sigma$ is proportional to $\Psi_0$.
- For high potential $\sigma$ rises more steeply than $\Psi_0$.
- The capacity $d\sigma/d\Psi_0$ grows with increasing surface potential.
- Depending on the salt concentration, the linear approximation (dashed) is valid till $\Psi_0 \approx 40\ldots80$ mV.

### 3.4.3.3. The capacity of the double layer

A plate capacitor has the capacity:

$$C = dQ/dU = \varepsilon\varepsilon_0 A/d$$ (3.67)

$Q$: Charge, $U$: Applied voltage, $A$: Area, $d$: Distance. The capacity of the electrical double layer per area is thus

$$C = \frac{d\sigma}{d\Psi_0} = \sqrt{\frac{2q^2 n_0 \varepsilon\varepsilon_0}{k_BT}} \cosh\left(\frac{q\Psi_0}{2k_BT}\right) = \frac{\varepsilon\varepsilon_0}{\lambda_D} \cosh\left(\frac{q\Psi_0}{2k_BT}\right)$$ (3.68)

It can be expanded $\cosh$ into a series ($\cosh x = 1 + x^2/2! + x^4/4! + \ldots$) and for small potential it can be broken off after the second term, then results:

$$C = \frac{\varepsilon\varepsilon_0}{\lambda_D}$$ (3.69)

### 3.4.4. Additional description of the electrical double layer

The Gouy-Chapman model is unrealistic for high surface potential $\Psi_0$ and small distances because then the ion concentration becomes too high. Stern tried to handle this problem by dividing the region close to the surface into two regions:

- The Stern-layer, consisting of a layer of ions, which as assumed by Helmholtz, are directly adsorbed to the surface.
- A diffuse Gouy-Chapman layer.

In reality all models can only describe certain aspects of the electrical double layer. The real situation at a metal surface might for instance look like in the following illustration.

![Diagram of double layer](image)

**Figure 3.4.3.:** Schematic representation of the double layer, Stern layer and diffusion layer (GC layer)

The surface potential, $\Psi_0$, is determined by the external potential and by adsorbed ions. These ions are not distinguishable from the metal itself (e.g. $Ag^+$ or $\Gamma$ on AgI). Next comes a layer or relatively tightly bound, hydrated ions (e.g. $H^+$ or $OH^-$ on oxides or proteins). If this layer exists it contributed to $\Psi_0$. The so called *Inner Helmholtz Plane, I.H.P.*, marks the centre of these ions. The Stern layer consists of adsorbed, hydrated ions. The *Outer Helmholtz Plane, O.H.P.*, goes through the centre of these ions. Finally there is the *diffuse layer*. The potential at the distance where it originates corresponds roughly to the *zeta-potential*. 