2.1. **Review of Colloidal Stability**

Colloidal dispersions are microheterogeneous systems in which a dispersed phase is uniformly distributed in a finely divided state throughout a continuous phase known as the dispersion medium. The precise meaning of finely divided is flexible, but the usual accepted size range for a colloidal particle is 1-1000 nm. While spheres are most often considered in modeling, colloidal dispersions of fibers, where only two dimensions fall into the colloidal range, and clay, where only one dimension may fall below 1 μm, are commonly found in important industrial applications. Thus, colloidal properties are observed when only 1 dimension falls into the colloidal size range.\(^1\)\(^-\)\(^5\) It is the size of the colloidal particles that lead to their unique properties.

Colloidal dispersions are known for their high surface-to-volume ratio. A high surface-to-volume ratio results in a significant number of the molecules in a particle lying at or near the surface. Thus, they are near or at the solid/liquid interface. The molecules at this interface have properties different from those of the bulk phases, and demonstrate the importance of surface chemistry in determining the properties of colloids.\(^1\) It is the material within a molecular layer of the solid/liquid interface which exerts the greatest influence on the particle-particle and particle-medium interactions. The amount of material needed to modify these interfaces and substantially alter the bulk properties is small regardless of the high surface-to-volume ratio. Therefore, it is the interactions in this molecular layer which we seek to understand and tailor with carefully designed additives to provide the appropriate level of stability when making a dispersion, and instability when weak flocculation is desirable, such as in many coating and paint formulations.\(^1\)\(^4\)\(^-\)\(^6\)
It can be shown from first principles that the free energy of two colloidal particles increases as the separation distance between their centers increases. Thermodynamically, all systems must minimize their free energy. Since for a colloidal system that would be zero separation distance between particles, the natural tendency of colloidal particles is to agglomerate. To prevent agglomeration, an energy barrier must be constructed that keeps the particles separated. This energy barrier must balance the force of attraction between particles with repulsive forces. Additives such as surfactants or polymers modify the solid/liquid interface such that an energy barrier is created and a metastable thermodynamic state is achieved.1-5,7

2.1.1. Intermolecular Potentials
The inherent attractive forces between non-polar particles were first observed by van der Waals in 1873. London showed that the forces arose from fluctuating dipoles within a molecule, and from quantum mechanics, he determined that they were proportional to the 7th power of the separation distance between the molecules

\[ F_{\text{att}} = -\frac{A}{r^7} \]  

[2.1.1]

By convention, attractive forces are negative and repulsive forces are positive. It follows upon integration of equation [2.1.2.1] with respect to distance that the work to reversibly separate the particles from a distance \( d \) to infinity is given as:

\[ \Delta G_{\text{att}} = -\Delta W = \frac{A'}{d^6} \]  

[2.1.2]

where the work at infinite separation is defined as 0. \( A' \) is a function of the polarizability, \( \alpha \), of the molecule and is defined for like molecules as:

\[ A' = \frac{3}{4} \hbar v \alpha^2 \]  

[2.1.3]
The term $\gamma$ is the frequency of the first ionization potential that lies in the UV region of the electromagnetic spectrum.

When the electron clouds of the atoms overlap, a short-range repulsive force is generated. This force, the Born repulsion, is given by:

$$F_{rep} = Be^{-ad} \quad [2.1.4]$$

where $B$ and $a$ are constants. The resulting potential energy is commonly approximated

$$\Delta G_{rep} = \frac{B'}{d^{12}} \quad [2.1.5]$$

The Lennard-Jones potential for describing the total interaction between 2 atoms is the summation of the attractive and repulsive energies given in equations [2.1.2] and [2.1.5].

$$\Delta G_{total} = \frac{B'}{d^{12}} - \frac{A'}{d^6} \quad [2.1.6]$$

It is seen that the van der Waals forces are long range in nature compared to the repulsive forces.1-5,7

2.1.2. Interparticle Potentials
2.1.2.1 Attractive Potential
The above describes the attractive forces between molecules or atoms. By treating the forces between two colloidal particles as the summation of the forces of the individual molecules composing the two particles, a similar result may be determined for colloidal
particles. For two infinite flat plates, a distance \( h \) apart, the free energy per unit area is given as:

\[
\Delta G_{\text{att}} = -\frac{A_H}{12\pi h^2} \quad [2.1.7]
\]

\( A_H \) is known as the Hamaker constant which for particles in a vacuum is given by:

\[
A_H = A \pi^2 q^2 \quad [2.1.8]
\]

where \( q \) is defined as the number of molecules in a unit volume of particles. For spherical particles of radius “a” such that \( h/a \ll 1 \)

\[
\Delta G_{\text{att}} = -\frac{A_H a}{12h} \left[ 1 + \frac{3H}{4a} + O(h^2) \right] \quad [2.1.9]
\]

Often, only the first term in equation [2.1.9] is necessary. Both cases demonstrate the fact that the attractive forces between particles are long-range forces, and thus the van der Waals type forces play a major role in determining the properties of a colloidal suspension. Hunter has compiled a table of force equations for different colloidal particle geometries of interest.\(^2\) Once the repulsive forces of the system, discussed below, are known, the total potential energy curve of the colloidal dispersion may be generated.

The derivations above are based on the assumption that the interactions occur instantaneously. The interactions take place at the speed of light and the assumption holds
at the atomic scale. On the colloidal scale, this is not an accurate description. The interactions of colloidal particles often occur at separations so large that the finite time required for photons to travel between them changes the functional form of equations [2.1.7] and [2.1.9]. In the case of flat plates, the decay increases to $h^{-3}$ from $h^{-2}$. Theories of colloidal stability account for this retardation effect, but for simplicity it is not necessary to include it in a discussion of the general principles of colloidal stability.$^{1-5,7}$

Attractive forces in a medium are lower than for a vacuum. The calculation of these forces has been a major topic of theoretical research aimed at describing the complex relationships between the particle and the dispersing medium. One useful approximation is the calculation of an effective Hamaker constant

$$A_{H}^{\text{eff}} = (A_{10}^\frac{1}{2} - A_{20}^\frac{1}{2})^2$$

[2.1.10]

where $A_{10}$ is the Hamaker constant for two particles of the dispersed phase interacting in a vacuum. Similarly, $A_{20}$ is for two particles of the medium interacting in a vacuum. Two important details in equation [2.1.10] are worth noting. First, the effective Hamaker constant is a square of the difference between the two Hamaker constants. The attractive forces for 1 in 2 will thus be related in the same manner. Also, as the properties of the particle approach those of the medium, the effective Hamaker constant decreases, and thus, the attractive forces decrease. The effect of the medium and the particle surface chemistry is demonstrated in Table 2.1.1.

Recalling that as the effective Hamaker constant increases, the attractive forces between the dispersed particles increases, one observes that the attractive forces for SiO$_2$ are 5 times higher in water than in octane. The polarity of water presents unique challenges for particle stabilization as will be discussed in later sections of this chapter. The particle surface chemistry is also a factor, as the Hamaker constant for TiO$_2$ in water is 26 times
Table 2.1.1. Hamaker constants for two media interacting across another medium (ref. 7).

<table>
<thead>
<tr>
<th>Particles</th>
<th>Media</th>
<th>$A_{\text{eff}} \times 10^{20}$ J</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>Water</td>
<td>1.0</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>Water</td>
<td>4.2</td>
</tr>
<tr>
<td>$\text{TiO}_2$</td>
<td>Water</td>
<td>26</td>
</tr>
<tr>
<td>Fused Quartz</td>
<td>Water</td>
<td>0.63</td>
</tr>
<tr>
<td>Fused Quartz</td>
<td>Octane</td>
<td>0.13</td>
</tr>
</tbody>
</table>

$A_{\text{eff}} = f(n_{\text{part}} - n_{\text{medium}}) = f(\varepsilon_{\text{part}} - \varepsilon_{\text{medium}})$
that of SiO$_2$ in water.$^{1-5,7}$

2.1.2.2. **Electrical Double Layer**

It has long been known that most colloidal particles are electrically charged, and in general, that at any interface between two phases there is a tendency for charge to accumulate. Wu has shown that when using a medium with a dielectric constant above 30, electrostatic effects become important.$^8$ These accumulated charges are balanced by the electroneutrality requirement such that the cations go to one phase and the anions the other. The surface charge on the particle, $\sigma_0$, is surrounded by a charge in solution equal in magnitude, but opposite in sign, $-\sigma_0$, called the countercharge. The combination of surface charge and countercharge form what is known as the electrical double layer. The accumulation of charge on a particle surface may occur in a variety of ways.$^{1-5,7}$ Five major mechanisms of surface charging are discussed below and are illustrated in Figure 2.1.1.

(i) **Ionization of surface groups**, Figures 2.1.1 (a) and (b). The dissociation of surface groups leads to charged surfaces. If the groups are acidic, a negatively charged surface is obtained. Conversely, a basic surface will yield a positive surface upon dissociation. The magnitude of the charge will depend on the relative strength of the acidic or basic surface group, and on the pH of the solution. Metal oxides in aqueous media may exhibit amphoteric behavior where both acidic and basic sites are obtained as the pH is varied.$^1$ The pH at which $\sigma_0 = 0$ is known as the point of zero charge, p.z.c. In the absence of specific adsorption, the point of zero charge is equivalent to the isoelectric point, i.e.p. The i.e.p. is the pH at which the electrokinetic or zeta potential, $\zeta$, is zero. The zeta potential is a measure of the charge located roughly one molecular layer into the medium. This layer, called the Stern or inner layer of the electrical double layer, will be discussed later in this chapter. If specific adsorption occurs, the p.z.c. and the i.e.p. move in opposite directions as the particle surface and thus $\sigma_0$ is altered by the adsorbed ions as shown in Figure 2.1.2. If enough adsorption occurs, the sign of $\sigma_0$ may be changed, as well.$^{2,3,5,7}$
Figure 2.1.1. Mechanisms for the origin of surface charges. (a) ionization of acid groups to give a negatively charged surface, (b) ionization of basic groups to give a positively charged surface, (c) differential solution of Ag\(^+\) from a AgI surface, (d) differential solution of I\(^-\) from a AgI surface, (e) isomorphous substitution in a clay surface to give a negatively charged surface, (f) breaking of a clay crystal to give a positively charged edge, (g) specific adsorption of a cationic surfactant, and (h) specific adsorption of an anionic surfactant. (ref. 1).
Figure 2.1.2. General appearance of the surface charge on oxides as a function of pH (a) specific adsorption of cations, (b) no specific adsorption, (c) specific adsorption of anions. (ref. 5).
(ii) Unequal distribution of lattice forming ions at the surface due to differential solubility, Figures 2.1.1 (c) and (d). When AgI is placed in water, dissolution occurs until the product of the ionic concentrations equals the solubility product.

\[ [\text{Ag}^+] [\text{I}^-] = K_s = 10^{-16} \quad [2.1.11] \]

If equal concentrations of the ions dissolve, no charge occurs on the surface. If Ag\(^+\) ions were added in the solution, one would reach the p.z.c. when the concentration \([\text{Ag}^+] = 10^{-5.5}\). The dissolution of Ag\(^+\) ions is suppressed. Adding more Ag\(^+\) ions would lead to charge reversal, as the I\(^-\) ions would dissolve preferentially. The surface charge is thus a function of the relative concentrations of Ag\(^+\) and I\(^-\) ions, and these ions are known as potential determining ions.\(^1\)-\(^3\),\(^5\)

(iii) Isomorphous substitution, Figure 2.1.1 (e). The exchange of a structural ion with one of lower valency as in a mineral surface. For example, the exchange of a surface Si by Al in a tetrahedral layer of clay results in a negatively charged surface.\(^1\)-\(^3\),\(^5\)

(iv) Charged crystal surfaces, Figure 2.1.1 (f). It is possible for a crystal platelet to be broken such that the edge may have a charge opposite that of the basal surfaces. For example, it is possible for a clay platelet to be broken such that a positive AlOH surface exists while the basal surfaces are negative. Each surface would thus have a different p.z.c., leading to unique colloidal properties, such as gel structures.\(^1\)-\(^3\),\(^5\)

(v) Adsorption of Specific ions, Figures 2.1.1 (g) and (h). These are ions which have an affinity for the surface of the particle which is not electrostatic or Coulombic in nature, but affect the charged structure of the solid/liquid interface without being considered part of the surface. These particles interact with the surface through relatively weak effects such as van der Waals forces, hydrophobic bonding, and hydrogen-bonding. For example, the
adsorption of an ionic group, such as a cationic surfactant leads to a surface charge reversal from negative to positive. For anionic surfactants, the sign of the surface charge would switch from positive to negative. It is the ability of the adsorbing ions to effect these types of changes, which promotes shifts in the p.z.c. and i.e.p. of the particle.\textsuperscript{1-3,5}

Indifferent ions interact with the particle surface through purely Coulombic interactions, and do not alter the location of the p.z.c. or the i.e.p. In the case of a metal oxide in aqueous solution, at pH < i.e.p. and low electrolyte concentration, $\sigma_0$ is positive. As the electrolyte concentration increases, a higher positive charge is observed. Similarly, at pH > i.e.p., a higher negative charge is observed as the electrolyte concentration increases.\textsuperscript{1-3,5} Only at the p.z.c., where electroneutrality exists, is the concentration of electrolyte immaterial.\textsuperscript{5} The interaction between the counterions and $\sigma_0$ and the effect of the counterions on the solution potential, $\psi$, will be discussed further in the section on double layer theory.

The nature of the surface is changed when an ion specifically adsorbs at the interface. A specifically adsorbing cation promotes OH\textsuperscript{-} adsorption, changing the net surface charge of the particle, $\sigma_0$. Thus, more H\textsuperscript{+} ions are required to neutralize the surface charge in the presence of the cation, and the p.z.c. shifts to lower pH. Similarly, a specifically adsorbing anion promotes H\textsuperscript{+} adsorption, shifting the p.z.c. to higher pH.\textsuperscript{19, 28, 29, 35} Figure 2.1.2 illustrates the effect of specifically adsorbing ions. The common intersecting points on curves for the specifically adsorbing ions now occur at pHs where the surface is still charged.\textsuperscript{5}

The electric double layer exists due to the charge separation at the solid/liquid interface. That is, the double layer consists of the surface charge and its compensating counter-ions. The counterions exist either in a mobile state due to thermal energy, the diffuse layer, or fixed near the surface in the Stern plane, as in the case of specifically adsorbing ions. The surface charge is thus balanced by the contribution of charge from the ions in the diffuse and Stern layers.
\[ \sigma_0 = \sigma_d + \sigma_s \]  

\[ \sigma_d \] being the charge in the diffuse layer, and \( \sigma_s \) being the charge in the Stern layer.

Boltzmann’s distribution law describes the probability of a particle being at a given point and having a free energy or potential energy \( V \) relative to a reference point. This law is derived from the chemical potential in terms of concentration for the electrostatic case of only counterions in solution. For positive ions:

\[ \mu = z_+ e \psi + kT \log c \]  

where \( z_+ \) is the valency of the positive ion, \( e \) is the elementary protons or electronic charge, and \( \psi \) the electrostatic potential. Then for some point in the solution there is a value of \( \psi \), such that the concentration of positive ions will be:

\[ c^+ = c^0 \exp\left(\frac{-z_+ e \psi}{kT}\right) \]  

where \( c^0 \) is the concentration of positive ions in a region where \( \psi = 0 \).

Similarly, for negative ions:

\[ c^- = c^0 \exp\left(\frac{-z_- e \psi}{kT}\right) \]
In this region there is then a net imbalance of charge that for a 1:1 electrolyte is described as:

\[
c^+ - c^- = c^0 \left[ \exp\left(\frac{-e\Psi}{kT}\right) - \exp\left(\frac{+e\Psi}{kT}\right) \right]
\]  \[2.1.16\]

An anion is surrounded by an excess of positive charge that forms what is called the charge cloud or ionic atmosphere, and an excess of negative charge surrounds a cation. For an electrically neutral solution, the net charge in the volume must be zero, thus:

\[
\int_{V_{\text{tot}}} [c^+ - c^-] dV = 0
\]  \[2.1.17\]

The above is the basis for the Debye-Hückel theory of electrolytes.\(^{1-3,5,7}\)

The ionic cloud is referred to as the electrical double layer. The charge on the particle is distributed over its surface and is just balanced by the total charge in the double layer in which there is an excess of counter-ions. This approach to describing a colloidal particle in electrolyte solution was first employed by Helmholtz, and later developed more fully by Stern and Guoy and Chapman.\(^{1-3,5,7}\)

Figure 2.1.3 illustrates three commonly encountered cases of electric double layers. For simplicity, the ions are represented as point charges with the exception of one ion in Figures 2.1.3 (a) and 2.1.3 (b) where diameters have been sketched to define the plane of closest approach to the surface. These planes are denoted with dashed lines at a distance, \(d\), in 2.1.3 (a) and \(\beta\) in 2.1.3 (b). In 2.1.3 (b), specific adsorption, the specifically adsorbed ions lie closest to the surface reflecting the short-range nature of the interaction.
Figure 2.1.3. Double Layer models: (a) no specific adsorption, (b) some specific adsorption, (c) superequivalent specific adsorption of anions. (ref. 5).
The plane defined by their centers and residing at $\beta$ is known as the inner Helmholtz plane, i.H.p. The plane at $d$, the boundary to the diffuse layer is known as the outer Helmholtz plane, o.H.p. The indifferent ions, having only Coulombic interactions with the surface, extend to greater distances into the diffuse layer. The charge density is high near the surface and falls off gradually as depicted by the solid curves in the figures. Also shown are the corresponding potentials due to the charged nature of the system. On the surface, the net charge, $\sigma_0$, results in a surface potential, $\psi_0$. Similarly, the Stern layer and diffuse layers have potentials $\psi_s$ and $\psi_d$, respectively. The value of $\psi_0$ is measured versus the solution, and with no net charge in the solid, it is constant.\(^5\)

In Figure 2.1.3 (a), the potential drops linearly through the Stern layer, then decays exponentially zero out into the diffuse region. With the addition of specific adsorbing ions, Figure 2.1.3 (b), linear decay in the i.H.p. and o.H.p. followed by exponential decay to zero into the diffuse layer. In addition, while $\psi_0$ remains constant, $\sigma_0$ is more positive due to the presence of the specific ions. The anions in the Stern layer screen the surface charge from the counter-ions in the diffuse layer. The length for decay to zero potential is shortened, as the double layer has been “compressed” due to the added ions.

Finally, in Figure 2.1.3 (c), the concentration of anions specifically adsorbed exceeds the net positive charge on the surface. Again, linear decay is observed in the Stern layer, but now it falls to a negative value and increases to zero in the diffuse region. This sign change of the potential in the Stern and diffuse layers is often called charge reversal. However, $\sigma_0$ is not only still positive, it is a higher positive value than in Figures 2.1.3 (a) or 2.1.3 (b), due to even better screening of the surface. The double layer is further compressed as well. The above model assumes that all surfaces are flat, charges are smeared out, and the layers are homogeneous.\(^5\)

The exponential decay depicted in Figure 2.1.3 is described as:
\[ \psi = \psi_0 \exp(-\kappa) \] \hspace{1cm} [2.1.18]

The Guoy-Chapman derivation of equation [2.1.18], using the Boltzmann distribution law and the Poisson equation, follows below.\(^5\) While derived for a symmetrical electrolyte, at low values of \(\psi_0\), it holds for asymmetrical electrolytes as well, e.g., 2:1 or 1:2 such as \(\text{CaCl}_2\).

The quantity \(\kappa^{-1}\), known as the Debye length, is the distance required for the potential \(\psi_0\) to decay to \(\psi_0/e\), and is considered to be the thickness of the double layer. It is given by:

\[ \kappa^{-1} = \left[ \frac{e^2}{\epsilon k T} \sum c_i z_i^2 \right]^{\frac{1}{2}} \] \hspace{1cm} [2.1.19]

As the concentration of electrolyte increases, the double layer thickness decreases, i.e. it is compressed. This explains the tendency of colloids to coagulate upon the addition of electrolyte to the dispersion.\(^1\,3\,5\,7\)

While the diffuse region controls particle interactions, its potential, \(\psi_d\), is determined by the stationary Stern layer. This potential cannot be directly measured. The zeta potential, \(\zeta\), is defined as the potential at the boundary where zero fluidity transitions to bulk fluidity, the slip plane. Electrophoresis and streaming potential are two types of electrokinetic experiments where the particles are subjected to tangential flows and \(\xi\) is measured. While the value of the zeta potential can be obtained, the exact location of the slip plane can not be established. However, experimental studies have shown that it is reasonable to approximate its location as equal to that of the o.H.p., and thus, \(\zeta = \psi_d\). This is an
important assumption in the theory of particle interactions and colloidal stability.\textsuperscript{5} From the above discussions, one can then picture a colloidal dispersion as a collection of charged particles, each surrounded by its own ionic cloud, such that when two similarly charged particles move towards each other, a repulsive force is generated as the tails of their double layers begin to overlap.\textsuperscript{1-3,5,7}

2.1.2.3. DLVO Theory
2.1.2.3.1 Original DLVO Theory
The fundamentals of the Deryagin-Landau-Verwey-Overbeek, DLVO, Theory have been described above. The original theory was derived for the contributions of van der Waals attraction and electrostatic potentials to the total energy curve.\textsuperscript{1-3,5,7} In this section, a further discussion of the theory will be presented.

While, empirically it had been known that colloidal stability was affected by electrolyte concentration, Schultz, in 1882, and Hardy, in 1900, concluded that the flocculation of a colloidal dispersion was in large part controlled by the nature of the ion of the added electrolyte. They observed that ion charge and valency were important factors in promoting instability in the colloid. Ions of the same charge were observed to have small effects regardless of nature or valency, and ions of opposite charge were observed to destabilize the dispersion. As the valency increased, the concentration of added electrolyte needed for instability decreased. The Schultz-Hardy rule states that the critical coagulation concentration, c.c.c., is primarily a function of the valency of the counterion. The c.c.c. is the minimum concentration of an added electrolyte which will promote rapid and therefore, irreversible, coagulation. The ratios determined in their experiments were 1:0.013:0.0016 for counterions of valency 1, 2, and 3, respectively. Within a valence level, other factors were important, and a ranking of ions was developed based on their effectiveness at promoting coagulation. For monovalent ions, Cs\textsuperscript{+} > Rb\textsuperscript{+} > K\textsuperscript{+} > Na\textsuperscript{+} > Li\textsuperscript{+}. Similarly for divalent ions, Ba\textsuperscript{2+} > Sr\textsuperscript{2+} > Ca\textsuperscript{2+} > Mg\textsuperscript{2+}. The electrostatic nature of colloidal stability was thus the obvious starting point for a theory to describe colloidal stability.\textsuperscript{1-3,5,7}

If equation [2.1.16] is multiplied by the valence of the counterion, the excess charge
density, \( \rho \), is obtained.

\[
z[c^+ - c^-] = \rho = zc^0[\exp\left(\frac{-e\Psi}{kT}\right) - \exp\left(\frac{+e\Psi}{kT}\right)] \tag{2.1.20}
\]

In this case, \( c^0 \) is now the bulk concentration of a \( z:z \) electrolyte. The Poisson equation relates \( \rho \) to the change in \( \psi \) with distance from the surface as:

\[
\frac{\partial^2 \psi}{\partial \kappa^2} = -\frac{\rho}{\epsilon} \tag{2.1.21}
\]

where \( \epsilon \) is the permittivity of the medium. Combining equations [2.1.20] and [2.1.21] yields the Poisson-Boltzmann equation which when solved for the case of a large surface potential at a point far from the surface where \( \frac{ze\Psi}{4kT} \ll 1 \), gives Equation [2.1.18].

The original DLVO theory assumed that the potentials for two overlapping double layers were additive. This implies that the electrostatic contribution to the free energy of interaction increases, and for two flat parallel plates, the total interaction potential energy, \( V_{\text{tot}}^{\text{int}} \), is:

\[
V_{\text{tot}}^{\text{int}} = V_{\text{el}}^{\text{rep}} + V_{\text{vdW}}^{\text{att}} = \frac{64c^0kT}{\kappa} \exp(-\kappa h) - \frac{A_H}{12\pi h^2} \tag{2.1.22}
\]

where \( V_{\text{el}}^{\text{rep}} \) is the repulsive energy due to electrostatic interactions and \( V_{\text{vdW}}^{\text{att}} \) is the attractive van der Waals potential defined in equation [2.1.7]. The repulsive term shows a dependence on electrolyte concentration through the exponential term, as from equation
[2.1.19] \( \kappa \) is a function of concentration. Therefore, increasing the electrolyte concentration results in a decrease in the energy barrier to coagulation.\(^1\)-\(^3\),\(^5\),\(^7\)

A rough approximation for determining the c.c.c. is to locate the point on the total interaction potential curve where both \( V_{\text{tot}}^{\text{int}} = 0 \) and \( \frac{dV_{\text{tot}}^{\text{int}}}{dH} = 0 \). Using these conditions with equation [2.1.22] yields:\(^1\)

\[
c^0(\text{c.c.c.}) \propto \frac{1}{A \kappa z^6} \tag{2.1.23}
\]

Of particular interest is the apparent agreement of the DLVO theory to the empirical Schultz-Hardy Rule. From the above approximation for \( c^0(\text{c.c.c.}) \), the DLVO theory predicts the concentration ratios of 1:0.016:0.0014 for ions with valencies of 1, 2, and 3, respectively, which agrees very well with the empirical values obtained by Schultz and Hardy. Unfortunately, the theory is derived for large potentials while flocculation occurs for low potentials, where a \( z^{-2} \) dependence is predicted rather than \( z^{-6} \). There are a number of assumptions made in developing the theory that may promote error in the limit of low potentials. For example, specific adsorption was neglected, but is known to occur for multivalent ions such as \( \text{Ca}^{2+} \) on certain surfaces.\(^1\)

2.1.2.3.2 Heterocoagulation
Heterocoagulation is an interesting phenomena observed in electrostatically stabilized colloidal systems. Heterocoagulation may be observed in two ways, when oppositely charged colloidal dispersions are mixed, and where small particles are mixed with large particles. For example, the mixing of metal oxide particles of sufficiently different i.e.p.s will result in the coagulation of the dispersion as observed for the first case. In the latter situation, the mixture of particles must have the same sign of charge and the potentials must be in a certain range. The values of the potentials, which will promote coagulation,
may be determined from equations [2.1.24] and [2.1.25] as a function of the separation distance. For particles of radius $a_1$ and $a_2$, and different surface potentials, the van der Waals forces may be approximated as:

\[
V_{vdW}^{\text{att}} = \frac{A_H a_1 a_2}{6(a_1 + a_2)h} \quad [2.1.24]
\]

when $2a_1 >> h$. The repulsive potential may be described as:

\[
V_{r}^{\text{rep}} = \frac{\pi \varepsilon_r \varepsilon_0 a_1 a_2}{a_1 + a_2} \left\{ 2 \psi_1 \psi_2 \ln\left[ \frac{1 + \exp(-\chi h)}{1 - \exp(-\chi h)} \right] + (\psi_1^2 + \psi_2^2) \ln[1 - \exp(-2\chi h))] \right\} \quad [2.1.25]
\]

where $\varepsilon_r$ is the permittivity of the solution phase and $\psi_1$ and $\psi_2$ are the potentials for particles 1 and 2, respectively.  

Several other trends predicted correctly by the DLVO theory are that the dispersion is harder to stabilize as the effective Hamaker constant increases, and the existence of a shallow secondary minimum in the total interaction potential energy curve. This is an important result as the secondary minimum may be specifically engineered to promote weak reversible flocculation which occurs at larger interparticle separations than rapid irreversible flocculation. Russell et al. have determined that a suitable depth of the secondary minimum, $V_{\text{min}}$, as a boundary between a stable dispersion and a weakly flocculated dispersion is roughly $2kT$.

2.1.2.4 Steric Stabilization
Steric stabilization arises from repulsive interactions between particles with adsorbed soluble layers of nonionic polymer or surfactant. The adsorbed materials establish a repulsive interparticle potential as a result of entropic effects and due to the segments desire to stay in solution, an enthalpic effect. Some literature describes polyelectrolytes as
providing steric stabilization in addition to electrostatic stabilization. In this chapter, steric repulsion due to a polyelectrolyte will be designated “electrosteric” as charged groups are used to promote adsorption on the particle surface. Nonionic surfactants and polymers adsorb via non-electrostatic mechanisms such as hydrogen-bonding or are grafted chemically onto the surface.\textsuperscript{1-3,5-7,9,10} An adsorbed, compact layer of thickness, $\delta_H$, which provides a hard sphere potential and does not get displaced upon collision with another particle, has the effect of preventing the centers of the particles from coming closer than $2(a + \delta_H)$, where “a” is the radius of the particle. The total interaction potential is described as:

$$V_{\text{total}} = \infty, \text{ when } h \leq 2(a + \delta_H)$$

$$V_{\text{Total}} = 0, \text{ when } h > 2(a + \delta_H)$$

[2.1.26]

In reality, the chains of the adsorbed layer do not behave as a hard surface, but may interpenetrate. The effect of chain interpenetration will be discussed in more detail later in this chapter.\textsuperscript{1-3,5-7,9,10} The density of the adsorbed layer is a key parameter in how the chains behave, as is the goodness of the solvent. Both determine how far the chains will extend into solution. The interpenetration of the chains, upon close approach of the two, coated particles, increases the local segment density of the polymer between the particles to a level higher than in the bulk. Hence, osmotic forces generated by the imbalance of chemical potential between the region between the particles and the bulk solution, push the solvent back into the region. This lowers the local segment density, restores the balance of chemical potential, and pushes the particles apart. In addition to osmotic forces, the interpenetration of the polymer segments constrains their mobility leading to a net decrease in the entropy of the system and therefore an increase of free energy. The need to increase the free energy of the system in order to interpenetrate results in a repulsive force. If a sufficiently dense layer is adsorbed, stability is maintained. A low layer density may not be sufficient for keeping the particles dispersed.\textsuperscript{1-3,5-7,9,10}
A key issue for designing a polymer for use as a steric stabilizer is to get good anchoring on the particle at high layer density, while also getting good chain extension into the medium. Because of the somewhat conflicting requirements of anchoring and chain extension, block copolymers are often used. Diblock copolymers have a structure of $A_nB_m$, where $A$ represents one type of polymer segments and $B$ a second type, for example, styrene-butadiene. Each block of segments is largely homogeneous in composition such that it retains the properties of its homopolymer analog. A block copolymer may be synthesized such that one block will adsorb onto the surface of the particle, the anchor block, and the other having a high affinity for the solvent will extend into solution, the tail block. Similarly, triblock copolymers, $A_nB_mA_n$, may be used. Further discussions of the adsorption properties and design of block copolymers will be presented later in this chapter.

The dispersion may flocculate if the solvent is altered in such a way that the “goodness” is lowered and the polymer chains collapse. This is commonly achieved by the addition of a non-solvent for the polymer. As the quality of the solvent decreases, the segment-segment interaction becomes preferred to medium-segment interactions until at the $\Theta$-point, the segment-segment interactions dominate. The $\Theta$-point marks the transition from a good solvent to a poor solvent for a given polymer. These interactions are characterized by the Flory interaction parameter, $\chi$. 

\[
\begin{align*}
\chi < 0.5 & \quad \text{good solvent} \\
\chi = 0.5 & \quad \Theta \text{- state} \\
\chi > 0.5 & \quad \text{poor solvent}
\end{align*}
\]  

As the solvent quality is lowered, the hydrodynamic layer thickness, $\delta_h$, decreases. As $\delta_h$ decreases, the repulsive potential is lowered until it can no longer balance the attractive
potential and flocculation occurs. As long as the adjustment to the solvent does not alter the Hamaker constant such that the attractive potential increases sufficiently to promote flocculation, a correlation between the Θ-point of the bulk homopolymer and that of the adsorbed stabilizer will be possible. 1-3,5-7,9,10

Temperature changes are a second route to reaching the Θ-point. Raising the temperature of the dispersion affects the interactions between the solvent and the polymer segments. For example, hydrogen-bonding interactions between a polymer and water decrease as the temperature increases. This net decrease in the segment-solvent interactions at some upper flocculation temperature, u.f.t., leads to segment-segment interactions and a smaller δH. This corresponds to the phase separation one would see for a polymer with a lower critical solution temperature. Similarly, a lower flocculation temperature, l.f.t., may be reached. 1-3,5-7,9,10

Bridging flocculation may occur when high molecular weight polymer is added to a suspension at sufficiently low concentration such that low surface coverage of the particles leads to the polymer chains adsorbing on more than one particle and binding them together. This type of behavior is used efficiently in water-purification where for example, a few ppm of high molecular weight polyacrylamide promotes the flocculation of particulates in the water. 1-3,5-7,9,10

An excess of polymer, either nonadsorbing or weakly adsorbing, may promote flocculation due to “depletion” of soluble polymer chains in the gap between particles. In depletion flocculation, as two particles approach each other, there will be a separation distance at which the free polymer in solution can no longer fit in the space between the particles and is expelled. The polymer concentration difference between the solvent in the gap and that of the bulk solution results in an imbalance of the chemical potential, and the solvent diffuses out of the gap drawing the particles closer together. This resulting osmotic pressure may be sufficient to promote flocculation of the colloid. 1-3,5-7,9,10 While the ability to flocculate the dispersion occurs for relatively low molecular weight polymer, the
volume fraction of polymer necessary to promote flocculation decreases as the molecular
weight increases.6

2.1.2.5 Total Potential Energy Curves
With knowledge of the attractive potentials and repulsive potentials of a colloidal
dispersion, it is possible to construct a total interaction potential energy curve by assuming
they are additive in nature.

\[ V_{\text{Total}}^{\text{int}} = V_{\text{vdW}}^{\text{att}} + V_{\text{BR}}^{\text{rep}} + V_{\text{el}}^{\text{rep}} + V_{\text{steric}}^{\text{rep}} + V_{\text{other}} \]  \[2.1.28\]

Usually only the repulsive terms due to electrostatic and steric contributions must be
considered, as they are the long-range potentials. The short range Born repulsion may be
ignored and often other effects are small or not apparent. Figure 2.1.4 shows typical total
potential energy curves for electrostatic and sterically stabilized colloidal systems. The
emphasis placed on the effects of electrolytes and layer density is due to the fact that they
determine the effectiveness of the stabilization method. In the case of electrostatic
stabilization, ionic impurities at low levels or small pH shifts may lead to irreversible
flocculation. These are common in many colloidal systems where metal oxide particles are
used.1

Recently, a short-range non-DLVO potential known to affect the total potential energy
curve was discovered. Called the hydration potential, it originates due to the hydration of
particles in aqueous media. This hydration layer gives rise to a force which acts over the
range of 1-2 nm. Although short range in nature, it is sufficient to promote stability, but
the dispersion may be somewhat flocculated.7

2.2. Surfactant Adsorption
2.2.1. Adsorption Isotherms
The Gibbs adsorption equation relates the amount of material adsorbed at an interface, \( \Gamma \),
Figure 2.1.4. Typical forms of the total interaction free energy for; (a) electrostatically stabilized systems, curves (i), (ii), and (iii) refer to increasing electrolyte concentration, (b) sterically stabilized systems, curves (i), (ii) and (iii) refer to constant density of polymer chains, but decreasing layer thickness decreasing medium goodness. (ref. 1).
to the surface tension of the interface, $\gamma$. For a mixture of $i$ components, it is written as:

$$-d\gamma = \sum_i \Gamma_i d \mu_i \quad [2.2.1]$$

where $\mu_i$ is the chemical potential of species $i$. $\mu_i$ is defined as:

$$\mu_i = \mu_i^* + RT \ln a_i \quad [2.2.2]$$

$\mu_i^*$ is the standard chemical potential and $a_i$ is the bulk activity of species $i$. $\gamma$ is described as:

$$\gamma = \left( \frac{\partial A}{\partial \Omega} \right)_{T,V,n_i} \quad [2.2.3]$$

where $A$ is the Helmholtz free energy of the system, $\Omega$ is the interfacial area, $T$ is the system temperature, $V$ is the volume of the system, and $n_i$ is the number of moles of species $i$ in the system. The Gibbs equation is valid for any interface. For dispersions of solids in liquids, $\Omega$ is usually large and adsorption is sufficiently high such that a measurable difference between the added concentration of adsorbent and the equilibrium concentration after mixing. For dilute solutions of adsorbent, where the chemical potential of the solid is assumed to be unaffected by the solution, the Gibbs equation may be rearranged and combined with a mass balance equation to give,
\[ \Gamma_a = \frac{(c_a - c_e)V_T}{m_p A_s} \]  

[2.2.4]

c_a is the added concentration of adsorbent (mass-volume\(^{-1}\)), c_e is the equilibrium concentration of adsorbent (mass-volume\(^{-1}\)), V_T is the total volume of solution, m_p is the mass of solid used, and A_s is the specific area of the solid (area-mass\(^{-1}\)). \( \Gamma \) will have units of mass-area\(^2\). Equation [2.2.4] is commonly used to calculate the adsorption isotherm.\(^1\)

A variety of methods for measuring adsorption isotherms have been developed and fall into two categories, direct and indirect. Indirect measurements are the most common and often easiest to perform. Changes in solution concentration may be detected by differential refractometry, NMR, UV absorbance if a chromophore group exists in the adsorbent, IR absorbance, and colorimetric methods. Direct methods are harder to perform or require more sophisticated equipment. These techniques include neutron reflectometry, evanescent wave methods, optical reflectometry, ellipsometry, NMR, surface plasmon resonance, surface-enhanced Raman scattering, and the quartz crystal microbalance.\(^10\)

2.2.2. Surfactant Adsorption

The discussion in this section is limited in scope as it is concerned with adsorption isotherm shapes and surfactant structures in solution. While there are analogies to polymer adsorption, the behaviors are significantly different. This work is concerned with the adsorption properties of polymers.

The word “surfactant” is an acronym for surface active agent as surfactant molecules are identified by their ability to adsorb strongly at an interface from a dilute solution. They have a water-insoluble tail, and a hydrophilic head group. The head group may be polar and thus nonionic, ionic, or zwitterionic. Surfactants form micelles in solution and often have formed complete monolayers of coverage on the interface at the critical micellar
The presence of adsorbed surfactant alters the interface. For example, if an oppositely charged surfactant adsorbs on a hydrophilic surface with surface charge $\sigma_0$, the surface is rendered hydrophobic when a monolayer of vertically oriented surfactant is adsorbed. On increasing the concentration of surfactant, further adsorption of a second layer changes the surface back to hydrophilic, but of opposite charge, $-\sigma_0$. Similar effects are observed with nonionic surfactants as well. The orientation of an ionic surfactant at the interface is a function of the electrostatic interactions and interactions such as, hydrogen-bonding, hydrophobic forces, and polar interactions. The presence of charged head groups plays an important role in the adsorption process as a result of lateral group repulsion. Any material which reduces head group repulsion, such as electrolyte or long chain alcohols, will enhance the adsorption process.\(^5\)

Figure 2.2.1 shows typical adsorption isotherms for sodium dodecyl sulfate, SDS, on several different carbon black surfaces from water. The curve for Spheron 6 carbon black rises gradually, then reaches an adsorption maximum called the adsorption plateau. The adsorption maximum occurs near the critical micellar concentration, c.m.c. The Graphon isotherm shows an inflection at low concentration then rises to a plateau again near the c.m.c. The inflection is believed to result from a two-stage adsorption process where the molecules initially lay parallel to the surface, then rearrange to a more vertical profile as the surface becomes crowded with surfactant molecules. Graphon is a heat-treated form of Spheron 6. Due to the heat treatment, it has a more homogeneous surface as compared to the Spheron 6, which contains oxygen complexes as well. The heterogeneous nature of the Spheron 6 may prevent an ordered layer at low concentration, thus no inflection point was observed. Finally, a curve for Graphon in the presence of $10^{-1}$ M NaCl shows a steep rise, no inflection, and an increased plateau value. These effects are all a function of the electrolyte concentration. The c.m.c. is lowered by electrolyte, thus, the plateau is reached at lower surfactant concentrations at higher ionic strengths. The higher plateau adsorption value is due to the electrolyte screening the lateral electrostatic repulsion of the
Figure 2.2.1 Adsorption isotherms for the adsorption of SDS onto carbon. The bottom curve is the Spheron 6/water, the middle curve is Graphon 6/ water and the top curve is Graphon/10^{-1} M NaCl interfaces. Arrow c.m.c. of SDS. (ref. 5).
charged head groups. Finally, the curve rises so steeply that the inflection point may not be observable. In summary, the surface structure, surface composition, and electrolyte concentration determine the nature of the surfactant adsorption.

For a surface where potential determining ions may alter the surface charge, the adsorption isotherm exhibits multiple regions. Figure 2.2.2 shows data for n-alkylsulphonates on alumina. Three distinct adsorption regions are observed. At low concentration, adsorption is promoted by ion exchange of the surfactant ions with indifferent electrolyte in the diffuse layer. As the concentration increases, adsorption increases rapidly, most likely a result of chain-chain interactions. These interactions may lead to a 2-D condensed surfactant aggregate, sometimes called hemimicelles, and as seen in the figure, adsorption increases as a function of increasing chain length. The third region is that at the point of charge reversal after reaching the i.e.p. The adsorption rate decreases because Coulombic forces now oppose adsorption above the i.e.p. The p.z.c. of the system was pH = 9, and the experiments were performed at pH = 7.2, below the p.z.c. It has been shown that adsorption of anionic surfactant will decrease by several orders of magnitude as the pH is adjusted to the p.z.c. From these results it is clear that specific interactions are not important in this system.

Nonionic surfactants may be treated broadly in terms of the surface type with Type I surfaces being hydrophobic and Type II surfaces hydrophilic. These two types of surfaces are unique in that the polar head group exhibits weak interactions with Type I surfaces and strong interactions with Type II. Figure 2.2.3 illustrates the mechanisms for adsorption on Type I and II surfaces along with the corresponding idealized adsorption isotherm.

The mechanisms are identical in each stage except that for a surfactant with strong interactions between the head group and the surface, adsorption levels above a monolayer are possible. The first stage of adsorption is parallel to the surface and a gradual increase in adsorption with concentration is observed. As more surfactant adsorbs, the surface becomes crowded exhibiting an inflection at possibly maximum parallel
Figure 2.2.2. Isotherms for the adsorption of sodium alkylsulphonates from aqueous NaCl onto alumina at pH = 7.2 and ionic strength $2 \times 10^{-3}$ mol dm$^{-3}$. Curves increase in alkyl chain length from the bottom as $C_{10}$, $C_{12}$, $C_{14}$, and top curve is $C_{16}$. (ref. 5).
Figure 2.2.3. Schematic representation of nonionic surfactants adsorption. Isotherm I and sequence I are for systems in which the headgroup/surface interactions are weak. Isotherm II and sequence II are for systems where the headgroup/surface interactions are strong. (ref. 5).
coverage, the molecules begin to orient in a vertical layer. The adsorption increases with concentration, again, until a monolayer of coverage is reached and the adsorption plateau achieved. In the case of strongly interacting head groups, the inflection point may not be observed, and the increase in adsorption with concentration is rapid once the molecules begin to orient in a vertical configuration. Adsorption beyond a monolayer occurs as the tails of the first layer interact with the tails in the second layer. Thus, a second monolayer may adsorb such that the head groups orient into the medium, and the tails orient towards the surface, as depicted. Regardless of the type of interaction between the surface and the surfactant, a large increase in adsorption near the c.m.c. is observed.\(^5\)

### 2.3. Polymer Adsorption

#### 2.3.1. Polyelectrolyte Adsorption

The sensitivity of polyelectrolytes to shifts in pH and ionic contamination is a serious limitation for their use in important aqueous industrial applications, such as ceramic processing and aqueous adhesive systems. As the focus of this work is on nonionic polymeric steric stabilizers for use in stabilizing submicron metal oxides in aqueous systems, only a brief discussion of polyelectrolytes will be given. The remaining sections on polymer adsorption and adsorption theory will be focused on nonionic polymers.

The behavior of charged polymers follows that of charged surfactants and homopolymer adsorption. Polyelectrolytes are widely used, especially on metal oxide particles where \(\delta_{H}\) larger than those feasible with surfactants is required. Figure 2.3.1 shows the behavior of an adsorbed polyelectrolyte versus increasing electrolyte concentration. The amount of adsorbed polymer, \(\Gamma\), increases with the increasing electrolyte concentration, as expected due to the electrostatic repulsion between chains being screened by the electrolyte. The increasing electrolyte concentration decreases \(\delta_{H}\) as shown in Figure 2.3.2. The double layer is compressed as the concentration of electrolyte increases, and thus, \(\delta_{H}\) decreases. These trends indicate the sensitivity of the polyelectrolyte to ionic contamination. Similar behavior is observed for changes in pH. Small shifts in pH or the presence of multi-valent ions can promote rapid irreversible coagulation.\(^5\)
Figure 2.3.1 Adsorption isotherm for poly(styrene sulphonate), $M_w = 780K$, absorbed onto negatively charged polystyrene latex at various ionic strengths. Circles are 0.1 M NaCl, filled triangles are 0.5 M NaCl, and squares are 1.0 M NaCl. (ref. 5).
Figure 2.3.2. Variation in $\delta_1$ with ionic strength for poly(styrene sulphonate), $M_w = 780K$, absorbed onto: open squares are negatively charged polystyrene latex, filled squares are positively charged polystyrene latex. Circles are values of $2r_G$ for solutions of poly(styrene sulphonate). (ref. 5).
2.3.2. Homopolymer Polymer Adsorption Theory
Polymer adsorption, like all spontaneous adsorption phenomena occurs when there is a net decrease in the free energy of the system. In the case of polymers, there is a balance between the enthalpy and entropy of the system due to the large number of segments in the polymer chain, and the loss of configurational entropy due to adsorption. Flory defined the interaction parameter, $\chi$, as:

$$\chi = \frac{[\varepsilon_{22} - \frac{1}{2}(\varepsilon_{11} + \varepsilon_{22})]z}{kT} \tag{2.3.1}$$

where $\varepsilon$ is the interaction energy between polymer segments and solvent molecules, 2 and 1, respectively. $z$ is the coordination number, $k$ is the Boltzmann constant and $T$ is temperature. $\chi$ describes polymer-solvent interactions.\(^5\)

Similarly, Silverberg\(^5\) defined the polymer-surface interactions in terms of the segmental interaction parameter, $\chi_s$, as:

$$\chi_s = \frac{\varepsilon_{2s} - \varepsilon_{1s} + \frac{1}{2}(\varepsilon_{11} - \varepsilon_{22})}{kT} \tag{2.3.2}$$

$\varepsilon_{2s}$ represents the interaction energy between the polymer segments, 2, and the surface, s. Similarly, $\varepsilon_{1s}$ represents the interaction energy between the surface and the solvent, 1. $\varepsilon_{11}$ and $\varepsilon_{22}$ are the interaction energies for the segment-segment interactions and solvent-solvent interactions, respectively. By this definition, $\chi_s$ is not a function of $\chi$ and the net change of energy upon adsorption of a segment is $\chi_s kT$. The term $\chi_s$ is the free energy penalty that a polymer segment must pay to compensate for the loss of configurational
entropy due to adsorption. Given this, polymer segments will either adsorb or be depleted at the interface, and the extent to which this occurs is determined by $\chi$. Above a critical value, $\chi_c$, adsorption occurs. If $\chi$ does not exceed $\chi_c$, the region near the interface has a lower concentration of polymer segments than the bulk solution. This region is depleted of polymer, a depletion zone. For an infinite molecular weight polymer, $\chi_c$ is only a function of the configurational entropy.\textsuperscript{5,10,11}

The factor $\chi$ and $\chi'$ were used by Scheutjens and Fleer in formulating the Self-Consistent Field, SCF, model. Numerical solutions to the free energy functions of a system may be obtained from this model, thus permitting the calculation of the adsorbed layer structure in terms of layer thickness, volume fraction of adsorbed chains, and the bound fraction of segments in the flat adsorbed trains, and nonadsorbed loops and tails.\textsuperscript{5,10} In this section, a general overview of the SCF theory, the tethered chain model of Russell et al., and the scaling theory of Marques and Joanny will be presented. The SCF theory is important in this work to understanding the physics of polymer adsorption. The combination of the tethered chain model and the scaling theory of Marques and Joanny, in addition to providing an understanding of the adsorption process, may be used to design a diblock copolymer for use as a steric stabilizer in aqueous media.

2.3.2.1 SCF Theory of Homopolymer Adsorption
Flory-Huggins used the concept of a lattice to describe polymer solution behavior, and the SCF theory is an extension of their model for inhomogeneous systems. In these models, space is discretized into layers or lattice sites. This reduces the infinite number of conformations in continuum space to a finite number that may be calculated. While continuum models are more general in nature, the ease of counting in the lattice model is desirable, but approximations in the counting statistics are necessary to evaluate chains in the polymer size range. In the case of the SCF theory, the excluded volume effects are only roughly estimated, and thus its predictions are most accurate as $\Theta$-conditions are approached.\textsuperscript{10,12}
Building on the work of Roe and Helfand who first developed lattice treatments for interacting chains in the 1970s using the mean field approach, Scheutjens and Fleer extended the mean field approach to account for all possible configurations, rather than just interactions in the region near the surface. As a result, the distribution of segments as a function of distance from the surface, and end segments are taken into account. As developed, the SCF model is capable of describing homopolymer, copolymer, polyelectrolyte, and tethered chain adsorption phenomena.\textsuperscript{10} The following discussion closely follows the treatment as given by Scheutjens and Fleer,\textsuperscript{10} and a review of the theory by Chen.\textsuperscript{12}

In the SCF theory, the polymer segments and solvent molecules reside on a lattice. The lattice, commonly depicted in two dimensions, but readily solvable in three, is divided into layers that lie parallel to the surface. The lattice is divided into $z$ layers containing $L$ sites each, the $z$th layer lying far from the surface in the bulk solution in the positive $z$-direction. If $i$ represents the layer, then starting at the surface, the lattice layers are numbered, $i = 1, 2, 3, \ldots, M$. The contents of each lattice site may be polymer segments or solvent molecules, but each site is of equal volume. Figure 2.3.3 illustrates the lattice construction. A lattice site has a coordination number, $w$, which accounts for the number of nearest neighbors. The bond weighting factors, $\lambda_o$ and $\lambda_1$ describe the nearest neighbor interactions. $\lambda_o$ accounts for the fraction of neighbors in the same layer, while $\lambda_1$ accounts for the fraction in adjoining layers. The total interactions subject to the constraint $\lambda_o + 2\lambda_1 = 1$. The volume fractions in each layer are described as $\varphi_i = n_i/L$ and $\varphi_i^o = n_i^o/L$, where $n_i$ and $n_i^o$ are the number of segments and solvent molecules in layer $i$, respectively. $\varphi + \varphi^o = 1$.\textsuperscript{10,12}

The SCF theory calculates the probability of every conformation in the lattice. A conformation is defined as the sequence of layers in which successive segments of chain are located. For any step of a component in the lattice, a weighting factor accounting for the average excluded volume and energetic interactions is used, subject to the constraint that all segments within the same layer have the same weighting factor. The weighting or
Figure 2.3.3. Typical conformation of adsorbed homopolymer chain in a lattice. The layer $i = 1$ corresponds to the chain in contact with the surface, while $i = M$ is representative of the bulk solution. (ref. 12).
where \( u(z) \) is the potential of a segment with respect to the bulk solution. For \( z \leq 0 \), \(-u(z)\) = \( \infty \) and \( G(z) = 0 \), and for large \( z \), \( u(z) = 0 \) and \( G(z) = 1 \). In the layer near the surface, \( G(z) \) is a function of the local concentrations, and thus, \( u(z) \) is a self-consistent potential that is a function of the energy parameters \( \chi_s, \chi_r \) and a hard core potential \( u'(z) \). \( u'(z) \) is the same for segments and solvent molecules and ensures that each lattice layer is full. Using a mean field approximation, \( G(z) \) may be found, as illustrated in the following discussion.\(^{10,12}\)

The volume fraction of segments in the \( z \)th layer is defined as \( \Phi(z) = G(z)\Phi^b \), \( \Phi^b \) is the volume fraction of segments in the bulk. The concentrations of middle segments, \( s \), in a chain of \( r \) segments that reside in the \( z \)th layer is determined from considering the joint probability that two walks, one of \( s-1 \) steps and another of \( r-s \) steps, both end in the layer \( z \). The contribution \( \Phi(z,s) \) of \( s \) segments in the volume fraction \( \Phi(z) \) in the \( z \)th layer is:

\[
\Phi(z, s) = \frac{C}{G(z)} G(z, s) G(z, r - s + 1) \quad [2.3.4]
\]

where \( C \) is a normalization constant derived from application to the bulk solution as:

\[
C = \frac{\Phi^b}{r} \quad [2.3.5]
\]
and $G(z)$ corrects for duplicate counting. Writing the above for any component $i$ in the system, the weighting function and segmental potential are written as:

$$G_i(z) = \exp\left(\frac{-u_i(z)}{kT}\right) \quad [2.3.6]$$

$$u_i(z) = u'(z) + u^{\text{int}}_i(z) \quad [2.3.7]$$

where $u_i(z)$ is the segment potential in the $z$th layer. $u_i(z)$ contains a hard-core potential $u'(z)$ which is independent of the segment type and has entropic origins, and an interaction energy, $u^{\text{int}}_i(z)$ that depends on the local concentrations and the interaction parameters $\chi$ and $\chi_s$. These potentials are defined in reference to the bulk solution in a manner such that they are excess quantities, with $u_i(\infty) = u'(\infty) = u^{\text{int}}_i(\infty) \equiv 0$. $u^{\text{int}}_i(z)$ is a function of the concentration profile, and thus is specified for each solution as required.$^{10}$

For a system of $s$ segments of component $i$, the end segment distribution $G_i(z,s)$ is:

$$G_i(z,s+1) = G_i(z)[\lambda_i G_i(z-1,s) + \lambda_d G_i(z,s) + \lambda_h G_i(z+1,s)] \quad [2.3.8]$$

which is written for a chain of $r$ segments as the recurrence relation:

$$G_i(z,s+1) = G_i(z) \langle G_i(z,s) \rangle \quad [2.3.9]$$
where $G_i(z,1) = G_i(z)$, $<G_i(z,s)>$ is a neighbor average value over three layers. Similar to the result for equation [2.3.4], the distribution $q_i(z,s)$ of segment $s$ in a chain of $r_i$ follows as:

$$q_i(z,s) = \frac{C_i}{G_i(z)} G_i(z,s)G_i(z, r - s + 1)$$  \hspace{1cm} [2.3.10]$$

where

$$C_i = \frac{\varphi_i^b}{r_i}$$  \hspace{1cm} [2.3.11]$$

For a monomeric solvent:

$$q_i = \varphi_i^b G_i(z)$$  \hspace{1cm} [2.3.12]$$

For polymer chains or oligomers:

$$q_i(z) = \sum_{s \neq 0} q_i(z,s)$$  \hspace{1cm} [2.3.13]$$
Finally, full occupancy of the lattice layers requires that

$$\sum \varphi_i(z) = 1 \quad [2.3.14]$$

Equations [2.3.6]-[2.3.14] form a self-consistent set of equations that are numerically solved to get the volume fraction distributions for the polymer and solvent molecules. The process is begun by guessing a form of \(u_i(z)\) for each \(i\), then solving for the each \(G_i(z,s)\). In summary, polymer adsorption in the SCF theory is a function of: 1) the polymer volume fraction in the bulk, \(\varphi^b\), 2) the chain length, \(r\), 3) the polymer-solvent interaction parameter, \(\chi\), 4) the segmental adsorption energy parameter, \(\chi_o\).

2.3.2.1.1. SCF Predictions

2.3.2.1.1.1. Chain Configurations

One significant prediction from this and other models of polymer adsorption and solution behavior is that polymer segment adsorption leads to three possible segmental conformations called trains, loops and tails. Figure 2.3.4 shows the differences in the structure of these conformations. Trains lie flat on the surface of the particle and dominate at low adsorption. Loops are multi-segment sections that rise off the surface, but are constrained at both ends. Tails are anchored to the surface, but have a free end in solution. At high surface coverage, the segments move towards the tail structure as the particle surface becomes crowded.\(^{10,12}\) Perhaps the most significant prediction of the SCF model is that it is the first model to predict tail extension at high values of adsorption.

2.3.2.1.1.2. Adsorbed Amount

Qualitatively, most of the adsorption theories that take into account chain interactions predict the same trends in adsorbed amount with chain length and solubility.\(^{10}\) The trends are that \(\Gamma_p\) increases with increasing chain length or degree of polymerization, \(r\), and increases with decreasing solubility. The SCF theory predicts that for a \(\Theta\)-solvent, \(\chi = \)
Figure 2.3.4. Segmental conformations for polymer adsorbing on a surface. Homopolymer and diblock copolymer adsorption is shown. Figures are drawn to indicate that layer thickness, $\delta_1$, is determined primarily by the tail segment conformation, and that $\delta_1$ for a diblock copolymer is greater for a corresponding homopolymer.
0.5, the plateau adsorbed amount, \( \Gamma_p \), increases linearly with \( \log r \) without bound. In a better solvent, such as an athermal solvent where \( \chi = 0 \), the slope (\( d\Gamma_p/d\text{MW} \)) and \( \Gamma_p \) are smaller. Figure 2.3.5 illustrates these results. Quantitatively, the predictions of Silverberg are different from those of the SCF model. Silverberg’s theory predicts an upper limiting value for \( \Gamma_p \) at infinite molecular weight in a \( \Theta \)-solvent.\(^\text{10,12}\)

The differences between the predictions for a good solvent and that of the poorer \( \Theta \)-solvent are observed to be a result of differences in the volume fraction of segments in loops. Figure 2.3.6 illustrates the predictions for the volume fractions of loops, trains, and tails as a function of the volume fraction of polymer in solution. This is an important result as the SCF model predicts that the hydrodynamic layer thickness, \( \delta_h \), a fundamental parameter in colloidal stability, is dominated by the volume fraction of the tails. Since \( \Gamma_p \) is a strong function of \( \chi \), but not of the fraction of tails, \( \delta_h \) is assumed to be less dependent on \( \chi \) than is \( \Gamma_p \). Figure 2.3.7 illustrates \( \delta_h \) for an athermal and a \( \Theta \)-solvent are indeed very similar.\(^\text{10,12}\)

The adsorbed amount may be defined in several ways. The excess adsorbed amount, \( \Gamma_{ex} \), is defined as the difference between the excess concentration of segments in each layer, \( \phi \), and in the bulk concentration, \( \phi^b \).

\[
\Gamma_{ex} = \sum_{i=1}^{M} (\phi_i - \phi^b) \quad [2.3.15]
\]

Figure 2.3.8 shows the dependence of \( \Gamma_{ex} \) on \( \phi_b \). The experimentally measured adsorbed amount, \( \Gamma \), is defined as the number of adsorbed molecules per surface site.
Figure 2.3.5. Trends for the plateau value of the adsorbed amount, $\Gamma_p$, as predicted by the SCF theory as a function of the degree of polymerization, $r$, for different values of $\chi$ and $\chi_0$. (ref. 12).
Figure 2.3.6. Fractions of trains, loops and tails for an athermal solvent, $\chi = 0$, and a G-solvent, $\chi = 0.5$, as a function of the volume fraction in the bulk, $\phi^b$, for $r = 1,000$ and $\chi_e = 1$. (ref. 12).
Figure 2.3.7. SCF predictions for the hydrodynamic layer thickness, $\delta_H$, as a function of the dimensionless adsorbed amount, $\Theta$, at various values of the degree of polymerization, $r$. Predictions are shown for the case of an athermal solvent, $\chi = 0$, and $\chi = 0.5$, a $\Theta$-solvent at $\phi^b = 10^{-2}$ and $\chi_s = 1$. (ref. 12).
Figure 2.3.8. SCF predictions for the adsorbed amount, $\Gamma_{ex}$, as a function of the volume fraction in the bulk, $\phi^b$, for an athermal and $\Theta$-solvent, $\chi = 0$, and $\chi = 0.5$, respectively. $\kappa = 1$. (ref. 12).
where $\varphi_i^f$ is defined as the volume fraction of chains in each layer not in contact with the surface or the volume fraction of free chains in each layer. In the surface layer, $\varphi_i^f = 0$, and in all other layers, $\varphi_i^f \leq \varphi^b$. Since $\Gamma_{ex}$ is the difference between the amount in the bulk and that on the surface, it underestimates the adsorbed amount, and $\Gamma_{ex}$ and $\Gamma$ are related as:

$$\Gamma = \Gamma_{ex} + \Gamma_d$$  \hspace{1cm} [2.3.17]

where $\Gamma_d$ is the amount of chains not in contact with the surface. If written in terms of equivalent monolayers, designated $\theta$, where $\theta = \Gamma/\Gamma_{mon}$, and $\Gamma_{mon}$ represents the adsorbed amount for monolayer coverage, then equation [2.3.17] becomes

$$\theta = \theta_{ex} + \theta_d$$  \hspace{1cm} [2.3.18]

Figure 2.3.9 illustrates the dependence of $\theta$ on chain length for several values of $\varphi$. $\theta$ increases as $r$ increases. At $\chi = 0.5$, and for $r \geq 50$, $\theta_{ex}$ and $\theta_d$ can be approximated as

$$\theta_{ex} = (1 - \varphi^b)(a + b \log r)$$  \hspace{1cm} [2.3.19]

$$\theta_d = \varphi^b(0.64 + 0.562r^{0.5})$$  \hspace{1cm} [2.3.20]
Figure 2.3.9. Dimensionless adsorbed amount, $\theta$, as a function of chain length, $r$, for bulk volume fractions, $\phi^b = 1$ and $\phi^b = 0.001$. The inset shows the qualitative trend for the segment concentration profile in the adsorbed layer. $\theta = \theta_{ex} + \theta_d$. (ref. 12).
The parameter, b, is a function of $\chi$, while the parameter, a, is a function of $\chi$ and $\phi^b$. For $r < 50$, $\theta_d$ is negligible compared to $\theta_{ex}$. $\theta_d$ is a function of r and $\phi^b$, only. For low $\phi^b$, $\theta \approx \theta_{ex}$ as $\theta_d \ll \theta_{ex}$. As expected for $\chi = 0.5$ and $\phi^b \rightarrow 1$, $\theta \approx \theta_d$ as $\theta_{ex} \rightarrow 0$. In this situation, only entropic effects are important, and adsorption decreases the configurational entropy of the polymer. $\theta \approx r^{0.5}$, the result for a Guassian distribution of chains in solution. For the case when $\phi^b \rightarrow 1$, $\theta_{ex}$ is small and the dependence of the system on $\chi$ is not important.$^{10,12}$

2.3.2.1.1.3. Dependence of the Adsorbed Amount on Concentration

Given the predictions for the conformation of the adsorbed chains and the review of surfactant adsorption as discussed in earlier sections, it is reasonable that a relation will exist between the adsorbed amount and the concentration. In the dilute regime, where the chains adsorb in flat trains, the relationship between $\theta$ and $\phi^b$ is: $^{12}$

$$\theta \propto \phi^b \cdot \exp[r(\chi + \lambda_d \cdot \chi)] \quad [2.3.21]$$

The SCF theory applies to the entire concentration range from very dilute to bulk polymer or $\phi^b = 1$. The SCF theory accurately predicts the high affinity type of isotherm observed for polymer adsorption, high affinity meaning that the initial slope of a $\Gamma$ versus $\phi^b$ curve is steep for low concentrations, $\phi^b < 10^{-6}$. The curve then levels off at a plateau region where the concentration in solution is measurable. In the very dilute region, the dependence of $\Gamma$ or $\theta$ on $\phi^b$ is linear as observed from equation [2.3.20]. Once enough chains adsorb they interact leading to the formation of loops and tails. This results in a decrease in the dependence on $\phi^b$, and a plateau is observed. While desorption of the chains is possible in very dilute solutions, polymer adsorption is practically irreversible by dilution due to adsorption kinetics being significantly faster than the kinetics of desorption. Desorption can be induced by changes in solvent goodness which may be due
accomplished by temperature changes or by modifying the solvent composition. Figure 2.3.7 illustrates how the \( \Gamma_{\text{ex}} \) varies with \( \varphi^b \). The distinct features of the curves are a gradual rise at low values of \( \varphi^b \) to a maximum at intermediate values of \( \varphi^b \), which is then followed by a decline to 0 at \( \varphi^b = 1 \).^{10,12}

2.3.2.1.1.4. Dependence of the Adsorbed Amount on \( \chi \)

According to the early theories and the SCF predictions, adsorption occurs when \( \chi > \chi_{\text{ec}} \). As \( \chi_{\text{ec}} \), can be shown to be approximately equal to \(-\ln(1-\lambda_i)\), it is easy to see that \( \chi_{\text{ec}} \) is often less than 1, given that \( \lambda_i = 0.25 \) for a hexagonal lattice. Figure 2.3.10 (a) shows \( \Gamma \) versus \( \chi \). It is clear from the figure that \( \Gamma \) is independent of \( \chi \) for values of \( \chi = 0.3 \). Between \( 0.3 < \chi < 2 \), the adsorbed amount is affected, but the strength of the effect is a function of the solvent-polymer interaction as described by \( \chi \). The curves of \( \Gamma \) are observed to climb steeply then level off to a plateau region as \( \chi \) approaches 2. For \( \chi \geq 2 \), high values, the adsorbed amount is weakly dependent on and \( \chi \). The direct surface coverage, \( \theta' \), is shown as a function of \( \chi \) in Figure 2.3.10 (b). \( \theta' \) is defined as \( p \cdot \Gamma \), where \( p \) is called the bound fraction. The bound fraction is defined as \( \Gamma_{\text{tr}} / \Gamma \), where \( \Gamma_{\text{tr}} \) is the adsorbed amount of polymer in trains on the surface. Thus, \( p \) is a measure of how strongly the chains are adsorbed on the surface. As \( p \) increases, the fraction of chains adsorbed as trains increases. Since trains lie flat on the surface, the adsorbed polymers are held tightly as many segments are adsorbed. As \( \Gamma \) increases, the number of segments per chain adsorbed decreases as more chains are adsorbed. The increase in the number of chains adsorbed leads to more loop and tail segments per chain. Thus, \( \Gamma \) is increasing, but the bound fraction is decreasing. From Figure 2.3.10 (b), it is seen that \( \theta' \) has the same dependence on \( \chi \) as \( \Gamma \), as expected.^{10,12}

2.3.2.1.1.5. Dependence of Adsorbed Layer Thickness, \( \delta_{\text{tr}} \), on \( r \), \( \varphi^b \), \( \chi \) and \( \chi_{\text{ec}} \)

The adsorbed layer thickness is a complex function of the polymer size, concentration, and solvent quality. In dilute solutions, low \( \varphi^b \) and \( \theta < < 1 \), \( \delta_{\text{tr}} \) is independent of the chain length, \( r \), since the adsorbed chains lay flat on the surface. As the concentration increases,
Figure 2.3.10. SCF predictions on a hexagonal lattice for (a) the adsorbed amount, \( \Gamma \), and (b) the direct surface coverage, \( \theta' \), as a function of \( \chi \) for athermal and \( \Theta \)-solvents, \( \chi = 0 \), and \( \chi = 0.5 \), respectively. \( \phi^b = 0.001 \). \( \theta' \) is a measure of how strongly the segments are bound to the surface. (ref. 12).
and hence the adsorbed amount, \( \delta_H \), increases. At high concentrations, a plateau is observed. Figure 2.3.7 shows \( \delta_H \) plotted versus \( \theta \). A steep rise in \( \delta_H \) is observed as \( \phi^b \) or \( \theta \) increases as the number of loops and primarily, the number of tails are increasing with increasing surface coverage. Since the length of the tails is a function of chain length, \( \delta_H \) is observed to increase with \( r \) as the concentration increases. The SCF theory shows that \( \delta_H \) is affected primarily by the fraction of tail segments. The increase in \( \delta_H \) is seen to occur at lower values of \( \theta \) as the solvent quality increases, thus as \( \chi \) decreases. In general, however, \( \delta_H \) is a weak function of \( \chi \). This is in agreement with the dependence of \( \delta_H \) on the fraction of tails as loops are a function of \( \chi \), but tails are relatively independent of \( \chi \). The increase in \( \theta \) in a poor solvent results from an increase in the number of loops. A slower increase in the tails is observed.\(^{10,12}\)

\( \delta_H \) is observed to be a weak function of \( \chi_s \), a result confirmed experimentally by van der Beek et al.\(^{13}\) He reported values similar values of \( \delta_H \) for SiO\(_2\) and cellulose esters in water. The interpretation of these results is significant when viewed with respect to results presented in Chapter 3, and the following discussion of acid-base interactions. In aqueous media, trends in adsorption behavior with polymer solubility are not necessarily the same as in non-polar solvents. The specific interactions of polar media with polymer chains are not well described by the original Flory-Huggins theory in which \( \chi \) was defined. The interrelation of acid-base mechanism and \( \chi \) is a potentially important issue in aqueous media.

2.3.3. Copolymer Adsorption
There are a variety of types of copolymers that may be synthesized, but with respect to colloidal stabilization, diblock, triblock, and graft copolymers are of particular interest. Most copolymers that are commercially available are nonionic in nature, thus there are no electrostatic contributions to the repulsive potential, only steric. While there are commercially available polyelectrolyte copolymers, they are usually alternating or random copolymers and their adsorption behavior is an average of that of their homopolymer
analogs. Nonionic random and alternating copolymers behave as an average of their homopolymer analogs as well. The most comprehensive review of block copolymer adsorption and homopolymer adsorption is the recent text by Fleer et al. The discussion below will focus on nonionic block copolymers.

Diblock and triblock structures take the ideal form of $A_nB_m$ and $A_nB_mA_n$, respectively. In this way, one may design a diblock or triblock such that one block will adsorb on the surface, the anchor block, and the other block will remain in solution, the tail block. The tail block is sometimes referred to as the buoy. In the case of a triblock, the center block is the anchor block and there are two tail blocks. The most widely studied triblocks are the Pluronic™ triblocks of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide), PEO-PPO-PEO. The anchor block may be soluble, and form a swollen layer resembling its homopolymer analog. The solvent in this case is referred to as non-selective. If the anchor block is insoluble, the solvent is called selective. In a selective solvent, the adsorbed anchor layer is collapsed, resembling a melt like film on the surface, while in solution, the anchor blocks may form micelles if their concentration is high enough. Figure 2.3.11 illustrates the adsorption of a diblock copolymer in a selective and non-selective solvent. Since the polymers in this study are fully soluble, the non-selective solvent predictions will not be discussed.

When optimized for steric stabilization, block copolymer adsorption is characterized at high surface coverage $\Gamma$ by the formation of a dense highly extended layer, called a brush. As $\Gamma$ increases, the anchor blocks adsorb and cover the surface. Eventually, the distance between tether points is so small that the tail blocks begin to interact. This crowding of the tail blocks leads to an imbalance of the chemical potential and a resulting osmotic pressure which repels the tails from each other and the surface into an extended state. As $\Gamma$ increases, the extension of the tail blocks increases until a brush, of thickness $\delta_b$, is formed.
Figure 2.3.11. Schematic illustrating an AB copolymer adsorbed on a surface from a non-selective solvent. \( d \) is the thickness of the adsorbed anchor block, and \( L \) is the thickness of the tail block. (ref. 12).
2.3.3.1 Scaling Theory for Non-Selective Solvent
Marques and Joanny\textsuperscript{16} have developed a scaling theory for describing the adsorption of a diblock in a non-selective solvent. The adsorption is distinguished by two distinct regions, the swollen anchor layer and the more dilute stretched buoy layer. The key parameter for each layer is the degree of polymerization of each block. If \( N \) represents the degree of polymerization of the polymer, where \( N = N_A + N_B \). \( N_A \) is the degree of polymerization of the anchor block, and \( N_B \) is the degree of polymerization of the tail block. We can define mole fractions for each block as \( \nu_A = N_A/N \) and \( \nu_B = N_B/N \), and thus, \( \nu_A + \nu_B = 1 \).

In considering the adsorption of the diblock, two situations are envisioned. When the anchor is small and tail is long, the tail interact leading to formation of the chain extended the brush layer. This limits the number of anchor segments adsorbed on the surface, leading to an unsaturated anchor layer. Increasing \( N_A \) leads to higher adsorption of the anchor due to the longer chains having higher adsorption energy than the smaller chains. This case is referred to as the buoy regime, as the tails dominate the adsorption. Figure 2.3.12 illustrates the buoy and anchor adsorption regimes. Fleer et al.\textsuperscript{10} have shown that the anchor block must have \( N_{\text{Tail}} \geq 30 - 40 \) and have a sufficiently high value \( \chi_6 \) so that it is not displaced by the tail block.

In the opposite case, where a large anchor block is present, the anchor segments interact on the surface, preventing the interaction of the tails. Little or no chain extension of the tail segments occurs. The anchor layer is saturated, with an essentially constant adsorbed mass of anchor segments. The reduced adsorbed amount, \( \Gamma \), means fewer adsorbed chains, which translates into fewer tail blocks. The lack of tail blocks and inability of the tails to interact results in a thinner adsorbed layer. This regime is known as the anchor regime as the anchor blocks determine the adsorption behavior.\textsuperscript{10}

The asymmetry ratio, \( \beta \), is a ratio of the occupied areas of the tail block and anchor block. In a non-selective solvent, this is a ratio of the square of the radii of gyration,
Figure 2.3.12. Illustration the anchor and buoy regimes of copolymer adsorption.
The transition from the buoy to anchor regime was determined to be a function of \( N_A \), \( \beta \approx N_A \). At low \( N_A \), and thus, low \( \nu_A \), the adsorbed amount increases as \( N_A \) increases. This is the buoy regime. For \( \beta < N_A \) and large \( \nu_A \), \( \Gamma \) decreases as \( N_A \) increases denoting the anchor regime. The theory predicts trends for \( \sigma \), the polymer surface density, which is the number of chains per unit area of surface. Given that the total adsorbed amount, \( \theta^a \), is defined as \( \theta^a = \sigma N \nu^2 \), it follows the same trend as \( \sigma \). Guzonas et al.\(^{11} \) have shown for polystyrene, PS, PS-PEO, diblocks adsorbing from toluene onto mica that \( \sigma \) is a function of the copolymer molecular weight, \( MW \) and the plateau value of the adsorbed amount. Toluene is a good solvent for both blocks. From this \( \sigma \) was calculated as:

\[
\sigma = \frac{\Gamma_p N_{AV} 10^{-21}}{MW} \tag{2.3.23}
\]

for \( \Gamma_p \) in mg/m\(^2\) and \( \sigma \) in nm\(^2\). \( N_{AV} \) is Avogadro’s number. This relation is useful as \( \Gamma_p \) is easily measured.

Summarizing the key trends from the MJ theory, for \( \beta > N_A \), buoy regime:

\[
\sigma \text{ or } \theta^a \propto \left( \frac{N_A}{N_B} \right)^{\nu_A} \left( \frac{1 - \nu_A}{\nu_A} \right) \tag{2.3.24}
\]
In the anchor regime, $1 < \beta < N_A$:

$$\delta \propto \frac{N_A^{\beta'}}{N_B^{\beta'}} = N_A \left(1 - \frac{1}{N_A}\right)^{\beta'}$$

[2.3.25]

$$\sigma \propto \frac{1}{N_A} = \frac{1}{N_A}$$

[2.3.26]

$$\delta \propto \frac{N_B}{N_A} \left(1 - \frac{1}{v_A}\right)$$

[2.3.27]

If $1/\sigma$ is substituted into equation [2.3.27], the predictions from the MJ theory agree with the scaling theory of de Gennes.\textsuperscript{10}

Chen et al.\textsuperscript{12} and Wu and coworkers\textsuperscript{8} have confirmed the predictions of $\delta$ by the MJ Theory for the anchor regime. Figures 2.3.13 and 2.3.14 illustrate their results. Similarly, Guzonas et al.\textsuperscript{11} found the predictions of the MJ theory to be useful for predicting the adsorption behavior of poly(ethylene oxide)-polystyrene copolymers.

Marques and Joanny have developed a scaling theory for diblock copolymers for brush formation in mediums where the anchor block is both soluble and insoluble. They have shown that brush formation is a sensitive function of the block length ratio $N_{Tail}/N_{Anchor}$, where $N$ is the degree of polymerization of the block. For the case of a soluble anchor block, the theory predicts a ratio that gives a maximum value of $\delta_H$ and $\Gamma$.\textsuperscript{10,16} The SCF theory predicts essentially the same conditions for brush formation, as will be discussed.
Figure 2.3.13. Linear relationship of surface density, $\sigma$, versus $N_A^{-1}$ for DMAEM-BMA adsorption onto Cab-O-Sil silica. Top curve is Chen et al.’s data. Bottom curve is a comparison of Chen et al.’s data to data of Wu et al. (ref. 12). The linear relationship of $\sigma$ versus $N_A^{-1}$, as predicted by MJ scaling theory for the anchor regime, is observed.
Figure 2.3.14. Comparison of the adsorbed layer thickness, $\delta_h$, data versus $N_B N_A^{-1/3}$ by Chen et al. (ref. 12) with that of Wu et al. (ref. 8). The linear relationship for $\delta_h$ versus $N_B N_A^{-1/3}$, as predicted by the MJ scaling theory for the anchor regime, is observed (ref. 12).
In addition, Fleer et al. have shown that the anchor block must have \( N_{\text{Tail}} \geq 30 \) - 40 and have a sufficiently high value \( \chi \), so that it is not displaced by the tail block.\(^\text{10}\) The scaling theory can be used to predict the diblock molecular weight and composition needed to stabilize a particle of a given type with a specified radius. One way to do this is to use the criteria for the depth of the secondary minimum of approximately \( 2kT \) as determined by Russell et al.\(^\text{9}\) This theory will be discussed later in this chapter.

The theoretical predictions discussed above are important results, as the advantages of block copolymer steric stabilization are industrially significant. The fact that high values of \( \chi \) are achieved with minimum overall molecular weight results in reduced cost of raw materials. The optimum amount for addition is easier to control than a corresponding polyelectrolyte, which minimizes the chance of depletion flocculation. In addition, as these polymers are nonionic, they are not sensitive to changes in pH or ionic contamination. These advantages result in improvements in processing.\(^\text{6,7,10}\)

### 2.3.3.2. SCF Copolymer Adsorption Theory

#### 2.3.3.2.1 SCF Theory Development

As copolymers, and in particular diblock copolymers, are more efficient as steric stabilizers due to their ability to form thicker adsorbed layers than homopolymers, their mechanisms for adsorption are of great interest. The theoretical approaches to describing copolymer adsorption are varied, and several theories are of particular interest in this work. This section will focus on the predictions from the SCF theory. Since random and statistical copolymers behavior is similar to that of homopolymers, and given the utility of diblock copolymers to this work, the discussion will focus on the SCF theory and how it pertains to diblock copolymers. As in the earlier section on SCF theory, this discussion will follow closely the description of the theory by Scheutjens and Fleer\(^\text{10}\) and the review by Chen.\(^\text{12}\)

The SCF theory for copolymer adsorption is an extension of the earlier theory for homopolymers, and thus the same considerations for constructing the lattice apply. Figure 2.3.15 shows a lattice for a diblock copolymer. As in the homopolymer treatment, all
Figure 2.3.15. Representative lattice construction for two $A_3B_5$ copolymers adsorbed on a surface. $i = 1$ when the polymer is in contact with the surface. For $i = M$, the polymer is in the bulk.
lattice sites are filled by solvent molecules or chain segments and each site has the same volume. The lattice is further defined by the lattice constants, $\lambda_0$, describing the fraction of nearest neighbor interactions in the same layer and $\lambda_1$, the fraction in adjacent layers. Each lattice site has $w$ nearest neighbors. This theory calculates the total number of configurations of the copolymer on or near the surface.

The term $\varphi_i^f(z)$ is defined to be the volume fraction profile of polymer chain molecules of type $i$ in the bulk, not on the surface. The volume fraction of adsorbed chains, $\varphi_i^a(z)$ is equal to $\varphi_i(z) - \varphi_i^f(z)$, where $\varphi_i(z)$ is the volume fraction of all chains segments of type $i$. $\varphi_i^a(z) \to 0$ far from the surface. The adsorbed amount, $\Theta$, was defined earlier as $\Gamma/\Gamma_{\text{mon}}$. $\Theta^a$ is thus the number of equivalent monolayers of $i$ segments adsorbed on the surface, which is computed by summing all $\varphi_i^a(z)$ in the lattice.

$$\xi_i = \sum_{z=1}^{N} \varphi_i(z) - \varphi_i^f$$

[2.3.28]

$\Theta^a$ is related to the adsorbed amount as:

$$\Gamma = \frac{\Theta^a \cdot MW_i}{A_i}$$

[2.3.29]

where $\Gamma$ has units of mass per area, $MW_i$ is the molecular weight of a segment of type $i$, and $A_i$ the area of a segment of type $i$. For a block copolymer, the $i$ segments would be segments in the anchor block of the polymer. The anchor block is the portion of the polymer chain designed to have an affinity for the surface. The anchor block is connected to the tail block, the portion of the chain that stays solvated.
2.3.3.3. SCF Copolymer Predictions

2.3.3.3.1. Effect of Chain Composition, Non-Selective Solvent

For a diblock copolymer composed of blocks of A and B type polymers, we define \( \nu_A \) and \( \nu_B \) to be the mole fractions of blocks A and B, respectively, in the polymer chain. As with such, then \( \nu_A + \nu_B = 1 \). Similarly, the segmental interaction parameters are \( \chi_{A_s} \) and \( \chi_{B_s} \). If we define block A as the anchor block and B as the tail block, \( \chi_{B_s} = 0 \) for the case where the tail block has no affinity for the surface. The SCF theory predicts a maximum in \( \theta^a \) as a function of chain length ratio of A and B, \( r_B/r_A \). Experiments by Wu et al.\(^8\) for poly(dimethyl amino ethyl methacrylate-b-n-butyl methacrylate), DMAEM-BMA, have confirmed the prediction that an optimum composition, \( \nu_A^{\text{opt}} \), exists for which the adsorption of A, and hence \( \theta^a \), is a maximum. Figure 2.3.16 (a) illustrates the maximum in \( \theta^a \) as a function of \( \nu_A \) and the total chain length r. The value of \( \theta^a \) is low initially due to the small number of anchor segments in the polymer, and thus a small adsorption energy. As the size of the anchor block is increased, the surface becomes fully covered in trains of A segments, leading to the maximum. Beyond \( \nu_A^{\text{opt}} \), the interaction between chains of A leads to loop and tail formation, effectively reducing the amount of adsorbed A segments in the total amount of A. The region to the left of the optimum is known as the buoy regime. That to the right is the anchor regime. It is important to recognize that both the SCF theory and MJ scaling theory predict a maximum in \( \theta^a \), separating the two regimes.

The SCF theory predicts that there is a relationship between the adsorbed amount ratio of copolymer A to homopolymer A as a function of \( \nu_A \).

\[
\frac{\xi^a}{\theta^{\text{hA}}} = (1 - \alpha) \nu_A + \alpha
\]  \[2.3.30\]

where \( \theta^{\text{hA}} \) is the adsorbed amount of A in the copolymer, \( \theta^{\text{hA}} \) is the adsorbed amount for homopolymer A, given that \( r_{Ac} = r_{Ah} \) where \( r_{Ac} \) and \( r_{Ah} \) are the degree of polymerization of
Figure 2.3.16. (a) Adsorbed amount, $\Theta^a$, in equivalent monolayers for diblock copolymers versus the mole fraction of anchor segments, $v_A$. Each curve represents a chain of constant total length, $r$. $\chi^b = 0.0001$, $\chi_{SA} = 2$, $\chi_{SB} = 0.5$, and athermal solvent for both A and B, $\chi_A = \chi_B = 0$. (b) The hydrodynamic layer thickness, $\delta_h$, as a function of the size of the tail block, $N_B$, for different solvent conditions, $\chi = 0.0$, athermal, $\chi = 0.3$, poorer solvent, and $\Theta$-solvent, $\chi = 0.5$. (ref. 12).
the copolymer A block and the homopolymer A. The term $\alpha$ is defined as $\lambda_{\alpha}(\chi_{BS} - \chi_{AA})$.

When $v_A = 1$, equation [2.3.30] reduces to the case for homopolymer A, and $\theta^a = \theta_{hA}^a$. Then, since $\theta_{hA}^a = \theta_A^a + \theta_B^a$ and $\theta_B^a = 0$ when only homopolymer A, $\theta_A^a/\theta_{hA}^a = 1$. For $r > 50$, where $r = r_A + r_B$ and $v_A > v_A^{opt}$, equation [2.3.30] may be rewritten in terms of the block ratio $r_B/r_A$, as $r_B/r_A = v_B/v_A$.

\[
\theta' = \theta_{hA}^a \cdot (1 + \alpha r_B/r_A) \tag{2.3.31}
\]

Assuming that, as $\theta_{hA}^a \to 1$, the total adsorbed amount of copolymer, $\theta'$, reaches the maximum value, then an estimate of the optimum mole fraction of A may be obtained.

\[
v_A^{opt} = \frac{1}{\theta_{hA}^a} \quad \frac{\alpha}{1 - o} \tag{2.3.32}
\]

Thus, $v_A^{opt}$ decreases as $\theta_{hA}^a$ increases, and the accuracy of the approximation improves as $r$ increases.

SCF theory predicts that the hydrodynamic layer thickness, $\delta_h$, will vary with $v_A$ in much the same way as $\theta^a$ is seen to vary. At values of $v_A > v_A^{opt}$, $\delta_h$ falls off more steeply than does $\theta'$. This is due to the sensitivity of $\delta_h$ to the extension of the tail block, and the SCF theory predicts that $\delta_h \propto r_B$, as shown in Figure 2.3.16 (b). $\delta_h$ is a weak function of the anchor block. Given that the SCF theory does not rigorously deal with the excluded volume of the of the system, the trends predicted are only qualitative. Again, it is significant that the trends predicted by the scaling theory are in agreement with those of
the SCF theory, which has been confirmed by experimental results of several authors.\textsuperscript{8,11,17}

2.3.3.3.2. Effect of Segmental Interaction Parameter, $\chi_{\alpha}$
Increasing $\chi_{\alpha}$ results in an increase in the adsorbed amount. Since the interaction of each segment of A is stronger as $\chi_{\alpha}$ increases, fewer segments are required for sufficient anchoring of the copolymer, and thus, $\nu_{A}^{\text{opt}}$ decreases. When the surface affinity is low, $\nu_{A}^{\text{opt}} \to 1$. Therefore, a critical value of $\chi_{\alpha}$ exists, below which the adsorption maximum does not exist, and the adsorbed amount continues to increase to a maximum for pure homopolymer A.

2.3.3.3.3. Effect of Solubility, $\chi$
As the solvent quality decreases, $\chi$ increases, and the adsorbed layer is compressed. This is expected as the affinity of the tail block for the solvent is decreased. Figure 2.3.16 (b) illustrates the dependence of $\delta_{t}$ on $\chi$. It is possible that the solvent quality may be used to promote adsorption of the anchor block. In Chapter 6, a study of the impact of anchor block solubility on adsorption is presented. In the study, the solubility of the anchor block was decreased by raising the temperature of the dispersion to near or above the cloud point of the anchor block. As the cloud point was approached, the anchor block solubility was decreased. Solubility near the cloud point was studied to determine if hydrogen bonding or insolubility of the anchor block would drive adsorption.

2.3.3.3.4. Effect of Chain Composition, Selective Solvent
The adsorption behavior of copolymers in a selective solvent is an entropically driven process. As micellar formation of the anchor block segments is likely in solution, the adsorption kinetics are more complex than those of the non-selective case. In addition, there is the possibility that above the critical micellar concentration, c.m.c., that the adsorbed species are themselves micellar. Another possibility is that no adsorption of polymer takes place. The adsorption of these diblock copolymers from selective solvents is more complex than the non-selective case, and as the polymers in this study fall into the non-selective category, no further discussion of selective solvent case is included. For
further details, the reader is referred to the work of Munch and Gast\textsuperscript{18,19} as well as Patel and Tirrell.\textsuperscript{20}

2.3.4 \textit{Terminally Anchored Chain Model of Adsorption}

The conditions for stability as developed in the terminally anchored chain model of Russell et al., provide a method for determining the thickness of a polymer layer necessary for the formation of a weak secondary minimum in the potential energy curve. This secondary minimum leads to phase separation in the colloid. When the minimum depth is on the order of 2kT, weak reversible flocculation occurs such that mechanical agitation or increased thermal energy redisperses the particles. The terminally anchored chain model is an ideal tool for determining size of the adsorbed layer needed for dispersing metal oxide particles in aqueous media. In this section, the development of the terminally anchored chain model will be presented. The discussion follows closely that of Russell et al.\textsuperscript{9}

2.3.4.1. Terminally Attached Chains, SCF Development

The conformation of a polymer chain attached to a surface by only one chain end has been shown by de Gennes and others\textsuperscript{10,21} to be a function of the surface density of terminally attached chains, \(n_p\), the size or degree of polymerization of the chain, \(N\), and the excluded volume, \(v/l^3\), where \(v\) is the excluded volume parameter, which accounts for pair interactions, and \(l\) is the length of a repeat segment of size \(N\). \(v\) is generally \(\leq l^3\). At the \(\Theta\)-state and in good solvents, as \(n_p\) increases, the interactions of the neighboring chains reduces the available volume of each chain, leading to the extension of the chains into solution, i.e. a brush layer. Figure 2.3.17 illustrates the case for isolated chains, low \(n_p\), and the case for brush formation due to interacting chains, high \(n_p\). The configurations of these chains may be calculated from continuum considerations of a self-consistent field approach in the manner of Dolan and Edwards.\textsuperscript{22}

Polymer chains are described by a density function, \(G(r, r', s)\), describing the number of configurations available to a subchain of \(s\) segments beginning at \(r'\) and ending at \(r\). Once \(G\) is known, the average configurations, total number of configurations, and mean-square-end- to-end distance may be determined, as well as the thermodynamic properties.
Figure 2.3.17. Conformation of terminally attached chains (a) isolated chains at low surface coverage. (b) interacting chains at high surface coverage. (ref. 9).
of the solution. In particular, the Helmholtz free energy, A, may be determined. A is of interest as it may be related to the Gibbs free energy and the pressure.

Dividing a chain of length N into subchains of length s and N-s, the probability of finding the sth segment at r for a chain beginning at r' and ending at r'' is proportional to G(r, r', s) G(r'', r, N-s). Integration over all possible endpoints along the chain and normalizing yields the local segment density,

\[
n(r) = \frac{n}{NW} \int_{0}^{N} G(r, r', s) G(r'', r, N-s) dr' ds' \quad [2.3.33]
\]

where \( n = \frac{NM}{V} \), the average segment density, M is the molecular weight of a repeat unit, V is the volume and W, the partition function for an individual chain, is defined as:

\[
W = \int [G(r, r', N) drdr'] \quad [2.3.34]
\]

G may be determined by realizing that at equilibrium the chain configurations are specified by:

\[
G(r, r', s) = \exp \left( -\frac{1}{kT} \int_{0}^{s} U(r(s')) ds' \right) \quad [2.3.35]
\]

U(r) is the segment potential accounting for interactions with all other segments, and the integral represents the internal energy of the chain. The expression implicitly takes into
account the configuration of all intermediate segments. Assuming U and G to be smooth functions, a differential equation for G may be derived subject to the condition that \( G(r, r', 0) = \delta(r - r') \). Where \( \delta \) is the Dirac delta function.

\[
\frac{\partial G}{\partial s} = \frac{l^2}{6} \nabla^2 G + \left[ 1 - \exp\left( \frac{U}{kT} \right) \right] \cdot G \tag{2.3.36}
\]

The first term describes the chain connectivity, the second term is the entropic contribution to chain dispersion, and the third term is concerned with the action of the potential U. Since U/kT determines the configurational density of the polymer chain, its choice is critical. U/kT > 0 reduces the local density of configurations excluding the chain from the region of space, while U/kT < 0 allows the chain in the region of space. A balance of the entropy and connectivity determines the configuration density when U/kT = 0. Following the derivations of de Gennes et al., Scheutjens and Fleer, and others, \(^{10,21}\) U/kT is described as:

\[
\exp\left( \frac{U}{kT} \right) - 1 = \frac{1}{kT} \frac{\partial f}{\partial n} \tag{2.3.37}
\]

where the free energy of segment-segment interactions, f, is defined in terms of the chemical potential, \( \mu \), and the pressure P as:

\[
f = \mu n - P - \frac{n k T}{N} \ln\left( \frac{n}{N} \right) - 1 = \left( \frac{1}{2} vn^2 + \frac{1}{6} wn^3 \right) kT \tag{2.3.38}
\]
Thus, equation [2.3.37] may be written:

\[
\exp\left(\frac{U}{kT}\right) - 1 = v_n + \frac{1}{2} w n^2
\]  \hspace{1cm} [2.3.39]

and the Helmholtz free energy may then be obtained as:

\[
\frac{A}{MkT} = \ln \left(\frac{n}{N}\right) - 1 - \ln W + \frac{1}{M} \int \left(\ln \frac{1}{1 + \frac{n}{W}}\right) dV
\]

\[
= \ln \left(\frac{n}{N}\right) - 1 - \ln W + \frac{1}{M} \int \left(\frac{1}{2} v n^2 + \frac{1}{3} w n^3\right) dV
\]  \hspace{1cm} [2.3.40]

Similar to \(v\), \(w\) is the triplet interaction parameter. \(w\) is dominated by the physical volume of the segments, thus \(w = l^6\). The integral in equation [2.3.38] corrects for over counting of configurations. The combination of equations [2.3.34], [2.3.35], and [2.3.36] constitutes a self-consistent mean field approach as the probability density \(G\) is related to the local segment density, \(n(r)\). This development is similar to the SCF model presented earlier in this chapter.

2.3.4.2. Terminally Anchored Chain Model, Isolated Layers

Given the high surface densities in the adsorbed layer, the segment densities are independent of the lateral position. This reduces the analysis of equation [2.3.34] to the 1-dimensional case.

\[
\frac{\partial G}{\partial \phi} = \frac{l^2}{6} \frac{\partial^2 G}{\partial \phi^2} + \left[1 - \exp\left(\frac{U}{kT}\right)\right] G
\]  \hspace{1cm} [2.3.41]
and

\[ n(x) = n_p \frac{\int_0^x \int_0^{x-s} G(x, x', N-s) ds dx'}{\int_0^x G(x',0,N) dx'} \]  \[ 2.3.42 \]

subject to the constraint

\[ G(x, x', 0) = \delta(x - x') \]  \[ 2.3.43 \]

where \( n_p \) is the surface density of chains. Solving for an expression for \( A \) gives:

\[ A = \frac{3}{kT} \left( \frac{L^2}{2Nl^2} + \frac{Nl^2}{L^2} - 2 + \frac{Nvn}{2} + \frac{Nwn^2}{6} \right) \]  \[ 2.3.44 \]

where \( L \) is the thickness of the extended chains attached at one end to the surface. The equilibrium condition for the layer thickness from the Gibbs-Duhem relation may be expressed as:

\[ \frac{\partial A}{\partial l} = \frac{L^2}{Nn_p} \frac{\partial A}{\partial L} = 0 \]  \[ 2.3.45 \]

given that \( nL = Nn_p \). Defining a dimensionless layer thickness, \( \alpha_0 = L/N^{0.5}l \), the
equilibrium condition may be rewritten in the familiar form:

$$
\alpha_0^2 - (1 + \frac{1}{7} \varphi_p^2) \alpha_0^2 = \frac{1}{\tau} z
$$

where the dimensionless surface density, $\varphi_p$, representing the volume fraction of segments that resides in a collapsed layer of thickness $l$, is defined as:

$$
\varphi_p = \frac{N_n \nu^0.5}{l}
$$

and $z$ is the ratio of the excluded volume per chain, $N^2 \nu$, to the volume occupied by the chain at ideal conditions, $N^{0.5}/n_p$. In the $\theta$-state, $z = 0$, and for $\varphi_p \leq 1$, $\alpha_0 = 1$. For $\varphi_p \geq 1$, and $\varphi_p^2 \gg 1$, the layer expands linearly with chain length or degree of polymerization, due to the physical volume of the chain segments. Similar results are seen in good solvents where $z \gg 1$. For good solvents, $\alpha_0 > 1$ and for poor solvents, $\alpha_0 < 1$.

2.3.4.3. Terminally Attached Chain Model, Interactions Between Layers

The above describes the chain configurations for polymer segments within isolated layers. For a colloidal system, the interactions of interest are those when the layers of any two particles interact. The theory must be extended to describe the interparticle interactions. When two such surfaces approach, the polymer layers first interact at separations on the order of twice the layer thickness. The volume available to each polymer chain is changed by the segment-segment and polymer-surface interactions, which in turn promotes a change in $A$. For $\nu > 0$, a repulsive force is generated due to the decreased number of configurations, and hence, higher free energy from the lower entropy associated
with the loss of volume as the layers interpenetrate. For \( v < 0 \), a net attractive force is generated from a volume increase per chain, and thus, a free energy increase. In either case, further reduction in the separation distance to less than one layer thickness, \( L \), results in a strong repulsive force.

Assuming a piecewise constant segment density in the gap between layers, the isolated chain analysis may be extended. Defining \( h \) to be the distance between particle surfaces, the equilibrium condition for the individual layers remains \( \partial A / \partial L = 0 \). Then, if \( h/2 \leq L \leq h \), the total concentration of segments has the form:

\[
n = \frac{N_n}{L^2} \left\{ \begin{array}{ll}
1 & 0 \leq x \leq h - L \\
2 & h - L \leq x \leq L
\end{array} \right.
\]

The free energy is then of the form:

\[
\frac{A}{kT} = \frac{3}{2} \left( \alpha^2 + \alpha^2 - 2 \right) + \frac{3}{2} \frac{z}{\alpha} \left( 1 - \frac{H}{\beta} + \frac{7 \varphi^2}{6} \right) \left( 1 - \frac{3 H}{7} \right) \]

where \( \alpha = L/N^{0.5} \). The equilibrium condition is then rewritten in terms of \( \alpha \) as:

\[
\alpha^3 - \left( \frac{7 \varphi^2}{9} \left( 1 - \frac{9 H}{14 \beta} \right) \right) \alpha^{-1} = \frac{1}{2} \left( 1 - \frac{2 H}{3 \beta} \right)
\]
where $H = h/N^{0.5}$. Comparing back to equation [.14], for large values of $h$, $\alpha \to \alpha_0$.

Finally, the interaction potential between two flat plates, $\Phi_{fp}$, is equal to the change in free energy per unit area. $\Phi_{fp}$ is written as:

$$\Phi_{fp} = 2n_p \left[ \Lambda(H, z, \varphi_p) - \Lambda_0(z, \varphi_p) \right] \quad [2.3.51]$$

Equation [2.3.47] and [2.3.48] may be used to determine $\Lambda(H, z, \varphi_p)$ and $\Lambda_0(z, \varphi_p)$ is determined from equations [2.3.42] and [2.3.44]. Remembering that the above derivation is for two flat plates, the Derjaguin approximation must be used to convert equation [2.3.49] to the more familiar sphere-sphere geometry for two spheres of radius $a$:

$$\Phi = \pi a \int_{r-2a}^{\infty} \Phi_{fp} dh - \frac{1}{6} \Lambda_{eff} \left( r-2a \right) \left( 2a^2 \frac{2a^2}{r^2} + \frac{2a^2}{r^2} + \ln \frac{r^2 - 4a^2}{r^2} \right) \quad [2.3.52]$$

where $\Lambda_{eff}$ is the non-retarded effective Hamaker constant which is determined from knowledge of the polarizability of the particle and the dispersion solvent. The argument, $r-2a$, is equivalent to $h$, the separation distance between the surfaces. $r$ is to the distance between particle centers. Solving equation [2.3.52] for $\Phi_{\text{min}}$ gives the criterion for the minimum layer thickness for stability. For a reversible weakly flocculated system, $\Phi_{\text{min}}$ should be around $2kT$. It is important to note that in deriving this stability criteria for phase separation, the steric forces are considered to be a function of only the excluded-volume.
For the situation where $\varphi_p = 1$, and $v = 0$, i.e. the $\Theta$-state. Under these conditions, full coverage and no excluded volume effects, the location of the secondary minimum stays the same for $r-2a = 2N^{0.5}l << 2a$, independent of the molecular weight. Given this, the criterion for the minimum layer thickness for stability may be generalized by evaluating the potential at $r-2a = 2N^{0.5}l$. Thus, setting the dimensionless potential minimum equal to 2 and solving yields:

$$-\Phi_{min} = \frac{A_{eff}(2N^{0.5}l)}{24kT} \frac{a}{N^{0.5}l} = 2 \quad [2.3.53]$$

rearranging and substituting for $A_{eff}(2N^{0.5}l)$ yields:

$$\frac{N^{0.5}l}{a} = \frac{0.57}{\Omega} \left( 1 + 0.014 \left( \frac{\Omega A_{eff}(0)}{kT} \right)^{\gamma_2} - 1 \right)^{\gamma_5} \quad [2.3.54]$$

where $A_{eff}(0)$ may be obtained from the literature or measured for different particle/solvent systems, $a$ is the particle radius, and $\Omega$, the dimensionless frequency characterizing retardation, is calculated from the relation:

$$\Omega = \frac{n_0 (\bar{n}_0^2 + n_0^2)^{0.5} a \omega}{c} \quad [2.3.55]$$

where $\bar{n}_0$ is defined as the low frequency limit of the refractive index in the visible range for the particle, $n_0$ is the same as $\bar{n}_0$, but for the solvent, $\omega$ is the most significant UV
relaxation frequency for the solvent, and \( c \) is the velocity of light.

Setting \( L \) equal to \( N^{0.5}l \), an estimate of the required layer thickness for stabilizing a dispersion in the weak secondary minimum of \( 2kT \) is obtained. \( L \) corresponds to \( \delta_H \), the adsorbed layer thickness mentioned earlier in Chapter 2. Appendix B contains a sample calculation illustrating the estimated layer thicknesses for various size alumina particles, assuming the adsorption of poly(2-ethyl-2-oxazoline) or poly(ethylene oxide) under \( G \)-conditions.

The calculations in this treatment require knowledge of the Kuhn length of the polymer, and an estimate of the adsorbed amount, \( \Gamma \), in order to calculate the degree of polymerization, \( N_{\text{tail}} \), of the copolymer and \( \delta_H \). Inputting the estimate of \( \delta_H \) from the terminally attached chain model into the scaling theory of Marques and Joanny, an estimate of the size of the tail and anchor blocks of a diblock copolymer for use as a steric stabilizer of metal oxide particles in aqueous media may be obtained.

2.4. **Substrate Chemistry**

The mechanism of interaction between a nonionic polymer and a metal oxide particle in aqueous media is an important issue. The factors influencing the adsorption of polymers from aqueous media are not as well understood as those for adsorption from organic solvents. In organic solvents, polymer insolubility drives polymer adsorption, as well as acid-base mechanisms.\(^{10,12,13}\) Figure 2.4.1 illustrates the results of studies by Killman et al.\(^{14}\) and Malmsten et al.\(^{15}\) with a commercial triblock copolymer used to disperse latex particles in organic solvents and water. In water, the insoluble poly(propylene oxide), PPO, block adsorbed onto the latex particles while the soluble PEO chains extended into the solution forming a thick steric barrier or brush structure. For an \( \text{SiO}_2 \) surface, the water-soluble PEO segments adsorbed rather than the PPO segments. A thin polymer layer was formed since the insoluble PPO segments did not extend into solution, and the particles were not well dispersed. Thus, insolubility of a polymer is not a sufficient driving force for adsorption on metal oxides in water.
Water-insoluble PPO anchor
Extended PEO tail
Hydrophobic latex surface in water
(Killman et.al. ‘88)

No PEO brush layer
Hydrophilic silica surface in water
(Malmsten, et.al.‘92)

Figure 2.4.1. Adsorption behavior of commercial nonionic polymeric surfactant of latex and SiO₂ particles.
Chen et al. proposed that PEOX adsorbs on SiO$_2$ due to hydrogen-bonding of the carbonyl carbon with the surface hydroxyls.\textsuperscript{12} Rubio and Kitchener,\textsuperscript{23} Koksal et al.,\textsuperscript{24} as well as van der Beek et al.\textsuperscript{13} discuss the inability of a polymer to adsorb on a surface from aqueous media. Rubio and Kitchner and Koksal et al., proposed that PEO did not adsorb on Al$_2$O$_3$ from aqueous media due to its inability to displace water molecules from the surface. PEO is known to form helices in aqueous media through hydrogen-bonding.\textsuperscript{15} Hydrogen-bonding, a form of acid-base interaction, is cited as a primary mechanism for polymer/substrate, substrate/solvent and polymer/solvent interactions in aqueous media.\textsuperscript{12,13,15,23,24} As mentioned in Chapter 1 and discussed in more detail in Chapter 3, PEOX adsorption on SiO$_2$, TiO$_2$, and Al$_2$O$_3$ appears to be driven by acid-base interactions.

Based on the work of Drago et al. and applying the Owens-Wendt equation for the work of adhesion, Fowkes et al.\textsuperscript{30,33,39} derived an expression for acid-base component of the work of adhesion. Based largely on the work of Fowkes et al., numerous experimental studies evaluating acid-base interactions at interfaces and implying the predominance of acid-base interactions to adhesion have been performed.\textsuperscript{25-38} Pocius points out, however, that no direct connection has been established to the adhesion forces at the interface.\textsuperscript{39} Jenson\textsuperscript{40} has reviewed the current models for acid-base interactions, and like Pocius,\textsuperscript{39} he concludes that experimental observations have driven an interest in acid-base interactions in adsorption and adhesion, but results have led to largely empirical relations rather than a fundamentally derived theory for acid-base mechanisms. It is feasible that the increasing sophistication of computer modeling of small molecules and polymer adsorption phenomena will improve the understanding of the role of acid-base interactions in adhesion and polymer adsorption.
REFERENCES


