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MASTER'S THESIS

Spontaneous dissolution of graphene in super acids investigated using mean field theory

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Abstract

Graphene and other allotropes of carbon, such as carbon nanotubes, cannot be dissolved in common solvents such as water or alcohols. Dispersion is possible with the use of surfactants, but this requires sonication. It was experimentally found that spontaneous dissolution is possible however in super acids, such as chlorosulfonic acid. From Raman spectroscopy measurements it is concluded that hydrogen ions, formed by the autodissociation of the acid, bind to Carbon atoms in graphene and carbon nanotubes and, by Coulombic repulsion cause a disjoining pressure that explains the dissolution. To validate this claim, we set up a mean-field theory using charge regulation to describe the disjoining pressure between platelets of graphene due to electric double layer interactions. We consider several complicating factors such as the image charge effect and the finite thickness of the graphene platelets. Our final conclusion is that, within the limitations of our model, double layer repulsions cannot explain the spontaneous dissolution of graphene in chlorosulfonic acid.

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Introduction

Graphene is what is called an allotrope of carbon consisting of a single layer of carbon atoms arranged in a hexagonal lattice. Other allotropes of carbon include for example graphite and diamond. Graphene needs no introduction. It has attracted large interest in recent years due to its remarkable physical properties, such as its extraordinary strength and high thermal and electrical conductivity. In one of the first publications on graphene in 2004, Geim *et al.* [1] demonstrated the ability to control the electronic properties of a few-layer graphene samples by an externally applied voltage, making it suitable for use in electronic devices. Graphene could potentially be used to manufacture more efficient solar panels [2], flexible and transparent screens in mobile devices [3] and even as a replacement for silicon in computer chips [4].

Because of the importance of graphene for both science and industry, finding an efficient means of production is of crucial importance. It is well known that carbon allotropes like graphite cannot be dissolved into graphene in common solvents such as water or alcohols. Dispersion is possible with the use of surfactants [5], but this requires sonication.

Over the years, several production methods for graphene have been developed, including so-called graphite oxide reduction [6]. As a first attempt, in 2004 Geim *et al.* used adhesive tape to split graphite into graphene [1]. Many of these production methods are reported to compromise the properties of the acquired graphene [7], yield low amounts or reduce the size of the acquired graphene flakes. Therefore, the quest to find a good production method for graphene remains an active one.

Exfoliation by superacids

In 2010 it was shown by Pasquali *et al.* [8] that graphite exfoliates spontaneously into single-layer graphene when immersed in chlorosulfonic acid. Concentrations as high as $\sim 2 \text{ mg ml}^{-1}$ were reported. It was shown that the acid disperses graphite from several different sources (such as graphoil and microcrystalline graphite) into graphene at high concentrations without the need for sonication. Chlorosulfonic acid is what is called a superacid, meaning it has an acidity greater than 100% sulfuric acid. Other superacids have been used to dissolve single-walled carbon nanotubes (SWNTs). However, chlorosulfonic acid seems to be the most promising candidate for dissolving both SWNTs and graphene into substantial concentrations. In this report we focus on the graphite/graphene system with its planar geometry and on its ability to dissolve in chlorosulfonic acid. Chlorosulfonic acid is a colourless or straw-coloured liquid consisting of tetrahedral molecules with formula ClSO₃H and was first produced by Williamson in 1854 [9] by the action of phosphorus pentachloride on concentrated sulfuric acid. It is a powerful acid that reacts explosively with water producing toxic fumes of hydrogen chloride and sulfuric acid. Chlorosulfonic acid has a high dielectric constant given by $\epsilon_r \approx 60 \pm 10$ [10,11], it goes by several other names, including chlorosulfuric acid, but we will refer to it by its most common name of chlorosulfonic acid, which we shall sometimes abbreviate to CSA.

Figure 1 is taken from the work of Matteo Pasquali and co-workers [8], and shows the spontaneous exfoliation of graphite into single-layer graphene in chlorosulphonic acid for varying acid strengths, obtained by mixing chlorosulphonic acid with concentrated sulphuric acid. The horizontal axis shows the volume percentage of chlorosulphonic acid in sulfuric acid. On the vertical axis, the Raman shift is shown. It is not important for this report to know the details of what the Raman shift means exactly, we can be satisfed by saying that it is a measure for the degree of solubility. It can be seen from the graph, and from the pictures in the insert, that the degree of solubility increases with increasing acid strength.



Figure 1: The Raman shift is a quantitative measure for the degree of solubility. Here it is plotted against acid strength for the chlorosulfonic acid dispersion of graphite. Acid strength is varied by mixing chlorosulfonic acid with sulfuric acid. The image in the insert shows the dissolution of graphite for different solvents. From left to right, graphite is dissolved in NMP(N-methyl pyrrolidone), 50, 65 and 80 vol% chlorosulfonic acid in sulfuric acid and finally in pure chlorosulfonic acid. Image taken from [8].

According to Pasquali *et al.* and also earlier works, the exfoliation of graphite in chlorosulfonic acid is due to protonation of the graphene layers: Hydrogen ions that form through the autodissociation of the acid bind to carbon atoms in graphene and hereby create a repulsive Coulomb interaction between the individual layers which drives them apart. However, it remains unclear how this process exactly occurs and how it can lead to exfoliation. In fact, it only explains the stability of the dissolved graphene layers in solution, not the process of exfoliation itself. In this report we attempt to describe the physics of this mechanism by using a mean field Poisson-Boltzmann theory. We attempt to construct our theory in such a way that the effect of acid strength, as well as several other physical parameters, including surface charge, on the solubility can be investigated theoretically.

Theoretical Description

Traditionally, a system of charged surfaces interacting through a liquid medium is described by DLVO theory, named after Boris Derjaguin and Lev Landau, Evert Verwey and Theodoor Overbeek. Our approach will be no different. DLVO theory combines attractive Van der Waals forces and the so-called double layer forces, which are of Coulombic origin and in general repulsive [12].

Van der Waals forces are well known. They are relatively weak and shortranged attractive forces between atoms, molecules and surfaces. Nevertheless, they play a vital role in describing the interaction of particles, especially at short range. The double layer interaction may require some explanation. A so-called electric double layer forms on the charged surface of an object if it is immersed in a liquid such as water or chlorosulfonic acid. The first layer consists of the surface charge itself, which is always localised at the surface. The second layer consists of counter ions from the liquid; they carry a charge opposite to the surface charge and are therefore attracted to the surface, but due to thermal motion also distribute themselves more or less evenly throughout space. The result is a well-localised surface charge and a diffuse layer of counter ions. Together they form the electric double layer, which has a typical thickness called the Debye length. The overlap of two double layers will, in general, produce a repulsive interaction between the charged surfaces.

Depending on the chosen physical parameters, the double layer forces have a much longer range than the Van der Waals forces. It is the combination of attractive Van der Waals forces and repulsive double layer forces that dictates whether two particles attract or repel each other. Physical properties of the system under investigation, such as acid concentration, surface charge and temperature determine the transition from repulsive to attractive interaction. The dependence of this threshold on the various physical parameters is one of the aspects investigated in this report.

There are several ways for the surface charge on our object to be described. One can, for example, assume either a fixed surface charge or a fixed surface potential. Both these assumptions make the model more readily solvable but they are often not very realistic physically. In general, physical objects such as colloids (and in our case flakes of graphene) have ionizable surface groups, meaning ions can either adsorb to, or dissociate from the surface. When immersed in an ionic solution, they therefore do not behave as insulators with fixed surface charge, nor as conductors with a fixed surface potential. Instead, both the surface charge and the surface potential are interdependent. This phenomenon is referred to as charge regulation [13]. The surface charge has to be determined from the surface potential, which follows from the solution of the Poisson-Boltzmann equation that in turn depends on the surface charge, making this a self-consistent problem.

Because of its planar geometry, our graphite/graphene system can be real-

istically described by a setup of two parallel plates. For this setup we solve the Poisson-Boltzmann equation for the case of charge regulation. We do so for the full nonlinear Poisson-Boltzmann equation, as well as the linearised version labeled the Debye-Hückel equation. We also study the so-called zero-field solution, which turns out to be both remarkably accurate and straightforward to solve for small particle separations. We aim to improve our results by considering two possible complications: First we will consider, instead of semi-infinite plates, two interacting membranes of finite thickness. This turns out to be of considerable importance for our particular setup. Second, we consider the issue of image charges: Objects, such as colloids usually have a much lower dielectric constant than the solvent in which they are immersed and this is certainly the case for our combination of graphene and chlorosulfonic acid. This mismatch in dielectric constants causes polarisation charges to form on the interfaces. The effect these polarisation charges have on our system can be represented by socalled image charges. We study two separate methods to describe the image charge effect.

From the Poisson-Boltzmann, Debye-Hückel and zero-field solution we shall determine physical quantities, such as the electrostatic potential, the ion densities and the effective surface charges of our system. Ultimately, we are of course interested in the interaction between the objects. We wish to determine under what conditions the objects repel and under what conditions they attract each other. This can be quantified by either considering what is called the disjoining pressure between the objects, or alternatively, the free energy of interaction. Both quantities are going to be determined and we demonstrate several methods of deriving them. The disjoining pressure due to the double layer forces turns out to show some unexpected behaviour for which we shall attempt to find a plausible explanation.

To conclude this introduction, we give a short outline of what to expect in this report. In Chapter 1 we give a detailed description of the electric double layer and find a solution for the electrostatic potential. Next, in Chapter 2 we introduce the theoretical setup of our model and look, in detail, at interactions between layers of finite thickness. In Chapter 3 we consider the image charge effect, by means of two different methods and look at Van der Waals forces as well as an alternative method of solving for the electrostatic potential, dubbed the zero field method. Chapter 4 is devoted to applying our theoretical results to the specific case of graphite dissolution in chlorosulfonic acid. Final conclusions and a short summary are given in Chapter 5.

Chapter 1

The electric double layer

In the introduction it was mentioned that the interaction between two objects immersed in a liquid, according to DLVO theory is governed by two types of force: The Van der Waals forces and the double layer forces. In this chapter we shall discuss the so-called electric double layer. A double layer forms on the surface of an object when it is immersed in a liquid. The object can be, for example a colloidal particle, a macromolecule like DNA, a virus, or in our case a flake of graphene. The solvent can be characterized, among other things, by its dielectric constant ϵ_r , temperature T and typically contains a certain concentration of both positive and negative ions. The solvent can, for example be water to which a salt like NaCl is added. The salt crystals typically dissociate and thereby introduce a certain concentration of ions into the liquid. In this report we consider the solvent (pure) chlorosulfonic acid which, through selfdissociation, introduces a certain concentration of ions in the solvent. At the moment however, it is not important where the ions originate from, we can be satisfied by considering a solvent that has a given concentration of positive and negative ions.

The object under scrutiny is considered to be large compared to the individual ions in the solvent. We will therefore not consider boundary effects and think of our object as a planar wall that extends to infinity in both directions. Also, we do not describe its inside region. At a later point in this report we examine whether the theory can be improved, by considering the inside region of the object to have a different dielectric constant than the solvent. For now we will only describe the region where the solvent resides, and assume that the dielectric constant of the object is similar to that of the solvent.

We imagine that the surface of the object acquires an electrical surface charge located at fixed sites, labeled 'S'. This can come about either because the surface is in contact with an external source of electrons or, more interestingly, when ions are adsorbed from the solution (or dissociated into the solution) on an initially uncharged surface. This procedure of either adsorption or dissociation of ions will result in the formation of a so-called double layer on the surface.

Imagine for example that the surface acquires a positive charge through the adsorption of positive hydrogen ions, a process called protonation. This layer is well-localised at the surface, with the protons being located at the fixed sites 'S'. Positively charged ions in the solvent will then be repelled from and negatively charged ions attracted to the surface. This movement of counterions in the solvent however, is counteracted by thermal motion, resulting in a negatively charged layer that is rather diffuse. It turns out that the second layer's profile can be described by the Boltzmann distribution, as will be derived in one of the next sections. The final result, consisting of the well-localized surface charge and the diffuse layer of opposite charge in the solvent, is what is called an electric double layer. The width of the double layer is characterised by the Debye screening length $\lambda_D = 1/\sqrt{8\pi\lambda_B n_b}$, where we have introduced the bulk ion density n_b and the so-called Bjerrum length $\lambda_B = \beta e^2/4\pi\epsilon_r\epsilon_0$. The Debye length is the most important length scale in DLVO theory, it is a measure of the screening of electric charge: With every Debye length the electric potential will decrease by a factor 1/e. It also means that when two objects approach each other to a distance less than about two Debye lengths, the overlap of their double layers causes an interaction between the objects: The double layer interaction. Figure 1.1 shows a schematic representation of a double layer on the planar surface of an object immersed in a solvent.



Figure 1.1: Schematic representation of a double layer on a single planar surface immersed in a liquid. The surface is located at z = 0 and is considered to have fixed sites S to which positive ions can adsorb. This creates a well-localized layer of positive surface charge. Counterions of negative charge are attracted to, and ions of positive charge repelled from the surface. However, due to thermal motion the second layer will be more diffuse. These two layers together form what is called the electric double layer. The width of the double layer is characterised by the Debye length λ_D .

As is common practice when studying a system of charged particles, we use Poisson-Boltzmann mean-field theory: Instead of describing the interactions between all the particles separately, we consider non-interacting particles in the presence of the mean field generated by all the other particles. As mentioned before, the ions in the double layer are distributed according to a Boltzmann distribution, derived in the next section using classical density functional theory. By combining the Boltzmann distribution and the Poisson equation, the Poisson-Boltzmann equation is obtained.

Several simplifying assumptions are made in our model. The ions are assumed to be point-particles and also the surface charge is described as being continuously spread across the surface instead of consisting of individual charges.

In this report SI units will be used. Where possible, we introduce dimen-

sionless units. A full list of variables and definitions used in this report is given in Appendix A.1.

1.1 The Poisson equation

Our starting point is the Poisson equation

$$\nabla^2 \psi(\mathbf{r}) = -\rho_e(\mathbf{r})/\epsilon_r \epsilon_0, \qquad (1.1.1)$$

where ψ is the electrostatic potential, ρ_e is the electric charge density, ϵ_r is the relative permittivity of the solvent and ϵ_0 is the permittivity of free space. If we then use the Bjerrum length, this can be written as

$$\nabla^2 \phi(\mathbf{r}) = -4\pi \lambda_B n(\mathbf{r}) = -4\pi \lambda_B (n_+(\mathbf{r}) - n_-(\mathbf{r})), \qquad (1.1.2)$$

where now $\phi = \beta e \psi$ is a dimensionless electrostatic potential and $(1/e)\rho_e(\mathbf{r}) = n_+(\mathbf{r}) - n_-(\mathbf{r})$ are the number densities of positive and negative ions respectively. The Bjerrum length λ_B defines a length scale for which the Coulomb interaction equals the thermal energy. Hence, it is a measure of the strength of the electrostatic interaction. Because our wall extends to infinity in the x and y directions, our problem reduces to a one-dimensional problem where the only spatial variable is the z-coordinate. The Poisson equation then becomes

$$\phi''(z) = -4\pi\lambda_B(n_+(z) - n_-(z)). \tag{1.1.3}$$

In the next section the Boltzmann distribution is derived.

1.2 The Boltzmann distribution

To derive the Boltzmann distribution we use a classical density functional theory, inspired by [14]. We start by writing down the functional for the Helmholtz free energy density

$$\mathcal{F}[n_{\pm},\sigma] = \frac{1}{\beta} \sum_{\alpha=\pm} \int_{-\infty}^{\infty} dz \{ n_{\alpha}(z) (\log[n_{\alpha}(z)\Lambda_{\alpha}^{3}] - 1) \} + \frac{1}{2\beta} \int_{-\infty}^{\infty} dz Q(z) \phi(z) + \frac{\sigma}{\beta} \{ \log[\frac{\sigma}{\sigma_{m}}] + \beta F_{b} \} + \frac{(\sigma_{m} - \sigma)}{\beta} \log[1 - \frac{\sigma}{\sigma_{m}}], \qquad (1.2.1)$$

where $Q(z) = n_+(z) - n_-(z) + \sigma \delta(z)$ is the total charge density consisting of the ions in the solvent and the surface charge, Λ_{α} is the thermal wavelength of the ions and F_b is a free energy of binding. F_b is the free energy associated with the binding of an ion to a site S on the surface. Finally, σ is the surface charge density and σ_m is the maximum surface charge density, when all possible sites S on the surface are occupied by ions. Note that \mathcal{F} is a free energy density per surface area.

Equation (1.2.1) contains several terms. The first term represents the ideal Helmholtz free energy of the ions, the second term the mean-field Coulombic

energy of the system, and the last two terms represent the free energy of coupling between the surface and the ions in the solvent. In Appendix A.2 we explain exactly how these different terms come about.

We further assume that our system is in osmotic contact with a reservoir that has particle density n_b for both positive and negative ions. The total ion density is therefore $2n_b$. It is then prudent to consider our system grand-canonically, via the following Legendre transformation

$$\Omega[n_{\pm},\sigma] = \mathcal{F}[n_{\pm},\sigma] - \int_{-\infty}^{\infty} dz \{ \sum_{\alpha=\pm} \mu_{\alpha} n_{\alpha}(z) + \mu_{\pm} \sigma \delta(z) \}, \qquad (1.2.2)$$

with the ion chemical potential given by $\mu_{\alpha} = (1/\beta) \log[n_b \Lambda_{\alpha}^3]$ for both positive and negative ions: $\alpha = \pm$.

The density profiles $n_{\pm}(z)$ minimize the grand potential Ω in thermodynamic equilibrium and should therefore satisfy the Euler-Lagrange equations. That is, we can minimize Ω with respect to $n_{+}(z)$ and $n_{-}(z)$ to obtain expressions for the ion distributions. The details of this derivation can be found in Appendix A.3. It finally leads to the celebrated Boltzmann distribution

$$n_{\pm}(z) = n_b \exp[\mp \phi(z)],$$
 (1.2.3)

which describes the distribution of the ions in the solvent, once the electrostatic potential $\phi(z)$ is known. Inserting the Boltzmann distribution in the Poisson equation gives us the Poisson-Boltzmann equation

$$\phi''(x) = \sinh[\phi(x)],\tag{1.2.4}$$

where we have now made the transition to dimensionless variables: $x \equiv z/\lambda_D$ by denoting our coordinate x in units of Debye lengths λ_D .

Equation (1.2.4) is our most important equation. It lies at the heart of the majority of results, presented in this report. It turns out however, that it can be solved analytically only for a few special cases, the setup with a single planar surface being one of them. If one considers, e.g. a spherical setup, or two parallel planar walls, no analytical solution is available and one has to resort to either numerical computation or use special functions to describe the solution. Therefore it can sometimes be insightful to look at the linearized version of equation (1.2.4) which turns out to be a good approximation if the (absolute) value of the potential $\phi(x)$ is small. The linearized Poisson-Boltzmann equation is more commonly referred to as the Debye-Hückel equation and given by

$$\phi''(x) = \phi(x),$$
 (1.2.5)

which is easily obtained from (1.2.4), by noting that $\sinh[x] \approx x$ for $x \leq 1$. A solution to the Debye-Hückel equation (1.2.5) is, in many cases more straightforward to obtain, as opposed to (1.2.4). We shall use the Debye-Hückel equation many times in this report, as a comparison to the nonlinear solution and sometimes to get a general idea of what a solution should look like, before looking at the more complicated nonlinear case. It turns out that the Debye-Hückel solution is a valid approximation if the dimensionless electrostatic potential has values up to $\phi \approx 1$, which corresponds to an electric potential of about 25mV under typical room temperature conditions. This statement is shown to be true in one of the next sections.

Both equations (1.2.4) and (1.2.5) are second order differential equations, meaning two boundary conditions are needed to solve them. Boundary conditions are the subject of the next section.

1.3 Boundary conditions and charge regulation

To be able to solve the Poisson-Boltzmann equation, two boundary conditions are needed. We can immediately write down the first boundary condition

$$\phi'(x \to \infty) = 0, \tag{1.3.1}$$

which is obviously true, if we consider our plane to be located at x = 0. Next, to find a second boundary condition we can either use Gauss's law, or we can consider the condition of charge neutrality. At this point, we use the latter method to obtain

$$\int_{0}^{\infty} dz (\rho_{+}(z) - \rho_{-}(z)) = -\sigma_{e}, \qquad (1.3.2)$$

where $\sigma_e = e\sigma$ is the surface charge density on the plate. This equation represents the statement that our total system must remain charge neutral: The total charge in the solvent must be equal and opposite to the total surface charge on the plate. Rewritten to our dimensionless variable x this becomes

$$\lambda_D \int_0^\infty dx (n_+(x) - n_-(x)) = -\sigma, \qquad (1.3.3)$$

where we have also used that $\rho_{\pm} = en_{\pm}$. By using the Boltzmann distribution for the ion densities $n_{\pm}(x)$ from (1.2.3) we find

$$\lambda_D n_b \int_0^\infty dx (\exp[-\phi(x)] - \exp[+\phi(x)]) = -\sigma.$$
(1.3.4)

From the definition of the Debye length we find for the bulk ion density $n_b = 1/(8\pi\lambda_B\lambda_D^2)$. We then multiply the entire expression by λ_B^2 to obtain

$$\frac{1}{8\pi\lambda}\int_0^\infty dx (\exp[-\phi(x)] - \exp[+\phi(x)]) = -\tilde{\sigma}, \qquad (1.3.5)$$

where we have defined $\tilde{\sigma} \equiv \lambda_B^2 \sigma$ and $\lambda \equiv \lambda_D / \lambda_B$ such that $\tilde{\sigma}$ is a dimensionless surface charge density and λ is a dimensionless variable that, among other less interesting parameters, relates to the bulk ion density and the permittivity of the solvent. By inserting the Poisson-Boltzmann equation from (1.2.4) we finally find

$$\phi'(x \downarrow 0) = -4\pi\lambda\tilde{\sigma},\tag{1.3.6}$$

where we have used the first boundary condition from (1.3.1) to compute the integral. This relation between the derivative of ϕ at the surface and the surface charge $\tilde{\sigma}$ in (1.3.6) must always be true. We can now consider three distinct surface conditions, leading to three different forms for the second boundary condition.

First, we can keep the surface charge density $\tilde{\sigma}$ in (1.3.6) fixed and use it as one of our input parameters. We will label this situation as FC for Fixed surface Charge. A second possibility is to keep the surface potential ϕ_s fixed and use it as one of our input parameters

$$\phi(x=0) = \phi_s. \tag{1.3.7}$$

This option is labeled FP for Fixed surface Potential. In general however, physical objects such as colloids (or, in our case platelets of graphene) have ionizable surface groups, meaning ions can either adsorb to, or dissociate from the surface. Therefore, they do not have a fixed surface charge, nor a fixed surface potential. Instead, both the surface charge and the surface potential vary interdependently. The surface charge has to be determined from the surface potential, which follows from the solution of the Poisson-Boltzmann equation which in turn depends on the surface charge, making this a self-consistent problem. This phenomenon is referred to as charge regulation and will be labeled CR for short in this report.

When considering the case of charge regulation we assume that only a fraction $\alpha \equiv \tilde{\sigma}/\tilde{\sigma}_m$ of available sites S on the surface is actually occupied by ions, which leads to the following form for the second boundary condition

$$\phi'(x \downarrow 0) = -4\pi\lambda \tilde{\sigma}_m \alpha, \tag{1.3.8}$$

where $\tilde{\sigma}_m$ now stands for the dimensionless maximum surface charge density, if all sites S were charged by the adsorption of ions.

To be able to move forward, we need an expression for α . One can be obtained by minimizing the grand potential Ω with respect to the surface charge σ : $\partial \Omega[n_{\pm}, \sigma]/\partial \sigma = 0$. The steps of this derivation are presented in Appendix A.4, it finally leads to the so-called Langmuir adsorption isotherm

$$\alpha = \frac{1}{1 + \exp[\beta F_b - \beta \mu_+ + \phi_s]},$$
(1.3.9)

where ϕ_s is the dimensionless potential at the surface $\phi_s \equiv \phi(x = 0)$. In Appendix A.5, an alternative expression for α is also derived by applying the law of mass action. This leads to

$$\alpha = \frac{1}{1 + K \exp[\phi_s]/n_b},$$
(1.3.10)

where K is defined as the surface dissociation constant for the chemical equilibrium $SP^+ \rightleftharpoons S + P^+$ between the surface and the ions in the liquid, such that

$$K \equiv \frac{[S][P^+]_s}{[SP^+]}.$$
 (1.3.11)

The square brackets represent concentrations; [S] stands for the concentration of empty sites S, $[P^+]_s$ represents the concentration of positive ions near the surface and finally $[SP^+]$ represents the concentration of sites that have been charged by adsorbing an ion. By comparing the two expressions in (1.3.9) and (1.3.10) we see that $K = n_b \exp[\beta F_b - \beta \mu_+]$. This provides us with a useful relation between the equilibrium constant K and the binding energy F_b . We shall introduce the dimensionless variable $r \equiv K/n_b$, called the surface reaction constant. From (1.3.10) we can obtain the following expression for r

$$r \equiv \frac{K}{n_b} = \left(\frac{1}{\alpha} - 1\right) \exp[-\phi_s] = \frac{\sigma_m - \sigma}{\sigma} \exp[-\phi_s], \qquad (1.3.12)$$

while α in this notation is given by

$$\alpha = \frac{1}{1 + r \exp[\phi_s]}.\tag{1.3.13}$$

We use r as a so-called fitting parameter to describe the adsorption of ions at the surface, when considering the case of charge regulation. More information about this is given in Chapter 4, when we consider the actual case of graphene dissolution in chlorosulfonic acid. For now, r will simply be used as one of our input parameters. Since α is defined as the portion of available surface sites that is actually ionized, it always take values between 0 and 1.

We now have a complete boundary value problem which can be solved to obtain the electrostatic potential. It consists of either (1.2.4) or (1.2.5), combined with boundary condition (1.3.1) and as a secondary boundary condition one of the expressions in (1.3.6), (1.3.7) or (1.3.8). In most cases, we use (1.3.8) as our second boundary condition and describe the case of charge regulation, as this is the most interesting and physically realistic surface condition. Also, the case of fixed surface charge can easily be obtained from it by setting r = 0.

1.4 Solution for a single double layer

We start by considering the most straightforward case, that of a single planar double layer. Consider a single planar surface, immersed in a solvent and located at x = 0, under charge regulation conditions. As mentioned before, we only consider the region x > 0, where the solvent resides. The complete boundary value problem is then given by

$$\phi''(x) = \sinh[\phi(x)]; \tag{1.4.1a}$$

$$\phi'(x \to \infty) = 0; \tag{1.4.1b}$$

$$\phi'(x \downarrow 0) = -4\pi\lambda\tilde{\sigma}_m\alpha. \tag{1.4.1c}$$

From the Poisson-Boltzmann equation and the boundary condition (1.4.1b) a general solution can be obtained,

$$\phi(x) = 2\log \frac{1 + C\exp[-x]}{1 - C\exp[-x]}.$$
(1.4.2)

By using the boundary condition (1.4.1c) and the expression for α from (1.5.4) we can obtain an expression for the integration constant C given by

$$\frac{4C}{1-C^2} = 4\pi\lambda\tilde{\sigma}_m \left[1 + r\left(\frac{1+C}{1-C}\right)^2\right]^{-1}.$$
(1.4.3)

The equation in (1.4.3) can, in principle, be solved analytically for C. The expression however is very lengthy and not particularly easy to work with. We

therefore choose to solve (1.4.3) numerically, to find an expression for C for given $\lambda, \tilde{\sigma}_m$ and r.

As mentioned in the previous section, we can also look at the linearised version of the Poisson-Boltzmann equation, commonly referred to as the Debye-Hückel equation

$$\phi''(x) = \phi(x); \tag{1.4.4a}$$

$$\phi'(x \to \infty) = 0; \tag{1.4.4b}$$

$$\phi'(x \downarrow 0) = -4\pi\lambda\tilde{\sigma}_m\alpha. \tag{1.4.4c}$$

The solution is straightforward and given by

$$\phi(x) = C \exp[-x],\tag{1.4.5}$$

where this time C is given implicitly by

$$C = \frac{4\pi\lambda\tilde{\sigma}_m}{1+r\exp[C]}.$$
(1.4.6)

Again, (1.4.6) and (1.4.5) together form the complete solution. We are now in a position to make a comparison between the Debye-Hückel solution and the full nonlinear solution, in order to check our statement from the previous section that the Debye-Hückel equation is a good approximation for values of the electrostatic potential up to $\phi \approx 1$. To this end, we will set r = 0, meaning we are considering a fixed surface charge, such that $\tilde{\sigma}_m = \tilde{\sigma}$. At this point it is convenient to introduce a new combined dimensionless parameter $\Sigma \equiv 4\pi\lambda\tilde{\sigma}$. Later, if we want to consider the influence of different parameters separately we can revert to denoting them individually, but for now a single parameter is more convenient.

In Figure 1.2, the electrostatic potential is plotted for various values of the parameter Σ . Several observations can be made from this plot. First of all, it can be seen that, for increasing Σ , the overall value of the potential increases. Remember that we defined Σ as $\Sigma = 4\pi\lambda\tilde{\sigma} = 4\pi\lambda_B\lambda_D\sigma$, meaning that it hides several physical parameters. For example, Σ is directly proportional to the surface charge density $\tilde{\sigma}$: $\Sigma \propto \tilde{\sigma}$, but inversely proportional to the square root of the bulk ion density: $\Sigma \propto n_b^{-1/2}$. One can therefore imagine increasing Σ by increasing the surface charge $\tilde{\sigma}$, while keeping all other parameters fixed. Furthermore, we can see that the linear Debye-Hückel solution gives acceptable results as long as $\Sigma \leq 1$ which, in this case also corresponds to $\phi \leq 1$. The first important result we can mention, is therefore that linear Debye-Hückel theory is valid when the dimensionless electrostatic potential $\phi = \beta e \psi \leq 1$. At a temperature of T = 293K this corresponds to an electric potential of about $\psi \approx 25mV$. This confirms the statement we made in Section 1.2. In general, linear Debye-Hückel theory overestimates the value of the potential when it reaches values beyond $\phi \approx 1$.

Beyond these observations, the single double layer setup does not offer very interesting physics, as there are no interactions involved. We therefore quickly turn our attention to a setup of two double layers in the next section.



Figure 1.2: The dimensionless electrostatic potential $\phi = \beta e \psi$ for a single double layer, for various values of the combined parameter $\Sigma \equiv 4\pi\lambda\tilde{\sigma}$, both from the full nonlinear Poisson-Boltzmann (PB) equation and the linear Debye-Hückel (DH) equation.

1.5 Two interacting double layers

At this point, we want to turn our attention to interacting objects. That is, we want to see what happens when two double layers start to overlap. We expect that the solution for the potential from overlapping double layers will not simply be given by the sum of the potential of two independent single double layer solutions. To find out whether this is indeed the case, we introduce the following model.

We consider two parallel planar surfaces of infinite thickness, separated by a distance d. The system is again considered to be in contact with a reservoir. The setup then looks as in Figure 1.3. To find the electrostatic potential, we have to write down a somewhat different set of boundary conditions as opposed to the setup with a single planar surface. The boundary condition at the surface remains valid, however, we can no longer specify the slope of the potential at large distance from the surface. Instead, by assuming mirror symmetry with respect to the plane at x = 0, we can infer that the slope of the potential midway between the planes is always zero. We therefore arrive at the following boundary value problem

$$\phi''(x) = \phi(x); \tag{1.5.1a}$$

$$\phi'(x=0) = 0; \tag{1.5.1b}$$

$$\phi'(x = \pm d/2) = \pm \Sigma_m \alpha, \tag{1.5.1c}$$

where, as a first attempt, we have written down the linear Debye-Hückel equation with charge regulation surface conditions and we have made the definition $\Sigma_m \equiv 4\pi\lambda \tilde{\sigma}_m$, analogous to the definition for Σ in the previous section. The



Figure 1.3: Our setup for two parallel plates. The plates are thought to extend to infinity in the directions perpendicular to the x-axis and have infinite thickness. The plates are separated by a distance $d = D/\lambda_D$.

general solution is given by

$$\phi(x) = C \cosh[x], \tag{1.5.2}$$

where the second boundary condition can be used to find an expression for C

$$C = \frac{\Sigma_m}{\sinh[d/2]}\alpha.$$
(1.5.3)

In Section 1.3 we already obtained an expression for α

$$\alpha = \frac{1}{1 + r \exp[\phi_s]}.\tag{1.5.4}$$

Now, we can find ϕ_s from the general solution for $\phi(x)$ by setting $x = \pm d/2$. When everything is put together, an implicit expression for C is found

$$C = \frac{\Sigma_m}{\sinh(\frac{d}{2})(1 + r\exp[C\cosh(\frac{d}{2})])},\tag{1.5.5}$$

which can be solved numerically. Together (1.5.2) and (1.5.5) form the solution for our two plate problem in the Debye-Hückel approximation.

Alternatively we can use the full nonlinear Poisson-Boltzmann equation to find the solution for the electrostatic potential. The method we are using here is inspired by [12] and [15]. Once again, all the steps to finding this solution can be found in Appendix A.6. It turns out that, in the nonlinear case, it is much more convenient to specify both ϕ and ϕ' at x = 0. We label the potential midway between the plates $\phi_m \equiv \phi(x = 0)$, as shown in Figure 1.4. This means that we start with the following set of equations

$$\phi''(x) = \sinh[\phi(x)]; \tag{1.5.6a}$$

$$\phi'(x=0) = 0; \tag{1.5.6b}$$

$$\phi(x=0) = \phi_m. \tag{1.5.6c}$$



Figure 1.4: In determining the electrostatic potential for the case of two electric double layers in the nonlinear approach, it is convenient to define the potential at the center between the plates: $\phi(x=0) \equiv \phi_m$.

From the Poisson-Boltzmann equation we find

$$\frac{d}{dx}\left(\frac{d\phi}{dx}\right)^2 = 2\sinh[\phi(x)]\frac{d\phi}{dx}.$$
(1.5.7)

This can be integrated once to give

$$\left(\frac{d\phi}{dx}\right)^2 = 2\cosh[\phi(x)] + C. \tag{1.5.8}$$

Using both boundary conditions we then obtain

$$\left(\frac{d\phi}{dx}\right)^2 = 2(\cosh[\phi(x)] - \cosh[\phi_m]), \qquad (1.5.9)$$

and the solution finally works out to

$$\phi(x) = 2 \operatorname{arcsinh}\left[\frac{\sinh[\phi_m/2]}{\operatorname{cn}(x \cosh[\phi_m/2], \frac{1}{\cosh[\phi_m/2]})}\right],\tag{1.5.10}$$

where arcsinh is the inverse hyperbolic sine and cn is one of the Jacobi elliptic functions, known as the Jacobian cosine amplitude. However, we do now have an expression for $\phi(x)$ as a function of ϕ_m . To obtain a full solution for $\phi(x)$, we need an additional expression to determine ϕ_m .

As before, we focus mainly on the charge regulation case. The additional expression we have at our disposal is the boundary condition that describes the relation between the slope of the potential at the surfaces and the surface charge density

$$\phi'(x = \pm d/2) = \pm \Sigma_m \alpha. \tag{1.5.11}$$

By inserting this boundary condition in (1.5.9) we obtain

$$\frac{\Sigma_m}{1 + r \exp[\phi(x = d/2)]} = \sqrt{2 \cosh[\phi(x = d/2)] - 2 \cosh[\phi_m]}, \quad (1.5.12)$$

where we have also used the expression for α from (1.3.10). Equations (1.5.10) and (1.5.12) together provide us with the complete solution for the potential $\phi(x)$ with input parameters Σ_m , r and d.

Now that we have an expression for $\phi(x)$, we are in a position to plot the electrostatic potential for varying values of the input parameters. We might, for example look at how the potential behaves as a function of plate separation. To this end, in Figure 1.5 we have plotted the potential for decreasing plate separation, ranging from d = 4 to d = 1. The solution from this section, for two interacting double layers is plotted and compared to the sum of the potentials from two independent double layers, one at x = -d/2 and one at x = d/2. It can clearly be seen that the overall potential increases for decreasing plate



Figure 1.5: The nonlinear (PB) dimensionless potential $\phi(x)$ for two interacting double layers compared to the sum of the potentials from two independent double layers (2P). Going from figure (a) to (d) the plate separation decreases from 4, 3, 2 to finally 1 times the Debye length λ_D . In all cases we have set $\Sigma_m = 1$ and r = 0, such that the surface charge is kept fixed.

separation, when the other parameters are kept fixed. Also, we can observe that the solution from the independent sum of potentials starts to deviate from the solution for interacting double layers, when plate separation is of the order $d \approx 2$ and smaller. This is exactly what we expect: Distance d between the plates is measured in units of Debye lengths, so when d = 2 there is a distance of $2\lambda_D$ between the plates. Since the Debye length is the characteristic thickness of the electric double layer, the two double layers begin to overlap when $d \approx 2$. It is clear from these plots that indeed, as we expected, considering two independent double layers does not lead to a correct determination of the electrostatic potential and one should use the solution for two interacting double layers instead.

Finally, we also want to look at the effect of varying the charge regulation parameter r. In Figure 1.6 the potential from the nonlinear solution is plotted for several values of the surface reaction constant r. It can be noted that, as



Figure 1.6: The dimensionless potential $\phi = \beta e \psi$ for two parallel plates in the case of charge regulation for various values of the surface reaction constant r, from the nonlinear solution. In all cases $\Sigma_m = 1$ and the distance between the plates is d = 5. The value r = 0 corresponds to maximum ionization of the surfaces.

the value of r increases, the overall value of the potential decreases. This is not unexpected and is a result of the lower value for the surface charge density. That this is the case can be seen by recalling the definition of r from (1.3.12),

$$r = \frac{K}{n_b},\tag{1.5.13}$$

where K is the surface dissociation constant for the chemical equilibrium $SP^+ \rightleftharpoons S + P^+$

$$K = \frac{[S][P^+]_s}{[SP^+]}.$$
(1.5.14)

If we imagine keeping n_b fixed, a larger value for r will result in a larger value for K and we expect the equilibrium to shift to a lower concentration of protonated sites SP^+ .

Chapter 2

Interacting membranes of finite thickness

In the previous chapter we set up our theory and found both the solution for a single planar object with a double layer, as well as for two planar objects with interacting double layers. Ultimately, we want to describe how separate layers of graphene, called platelets, are dissolved in chlorosulfonic acid. A platelet of graphene is very thin, only one layer of atoms thick. Compared to its thickness, its other dimensions can thus be considered very large. We therefore consider in this chapter a setup that more closely resembles the physical properties of the system we are describing. That is, we consider the objects to be of finite thickness, dubbed membranes. In Chapter 1 we already looked at two interacting plates that have infinite thickness, now we want to see what effect the finite thickness of the object has on the potential profile, ion densities and ultimately, the interaction between the objects. The finite thickness of the membranes implies that now we must also describe the outer region, where solvent resides as well. We start in the next section by setting up our model, which was inspired by [15].

2.1 Setting up the model

We consider the model as shown in Figure 2.1. It consists of two membranes of finite thickness, placed a distance d apart and having thickness h. Both d and h are dimensionless variables, measured in units of Debye lengths, such that $d = D/\lambda_D$ and $h = H/\lambda_D$. We imagine the membranes to extend to infinity in directions perpendicular to x and the entire system is thought to be in contact with a monovalent salt reservoir, as before. At the moment we assume that the membranes consist of a medium that has the same dielectric constant as our solvent, to avoid the effect of image charges. The image charge effect is considered in Chapter 3.

When the membranes are immersed in a solvent, we expect electric double layers to form on all four surfaces. When the membranes are far apart, no difference between the inner and outer surfaces is to be expected. However, as the membranes move closer together, the inner double layers will start to interact and, as a result a discrepancy between the inner and outer surfaces



Figure 2.1: Two membranes of finite thickness, immersed in a solvent. The membranes are separated by a distance d and have thickness h. As before, the system is connected to a reservoir that has a given density of both positive and negative ions.

might very well develop. We do however assume mirror symmetry with respect to the plane x = 0. All results in this section were obtained using the nonlinear Poisson-Boltzmann equation.

We can now divide space into five regions and write down the expressions for the electrostatic potential in each of them. The five regions of our system will be denoted with Roman numerals as follows.

 Region I:
 x < -d/2 - h;

 Region II:
 -d/2 - h < x < d/2;

 Region III:
 -d/2 < x < d/2;

 Region IV:
 d/2 < x < d/2 + h;

 Region V:
 x > d/2 + h.

Because there are no charges inside the membranes, the electric field is constant and the electrostatic potential can be described by a linear expression ax + b. For the outside regions, the solution for a single electric double layer can be applied, while for the inner region we can use the solution for two interacting double layers, both of which were found in Chapter 1. The solutions for the five regions we defined are then given by

$$\phi_I(x) = 2\log\left[\frac{1+a_1\exp[x+d/2+h]}{1-a_1\exp[x+d/2+h]}\right];$$
(2.1.1a)

$$\phi_{II}(x) = a_2 x + a_3; \tag{2.1.1b}$$

$$\phi_{III}(x) = 2 \operatorname{arcsinh}\left[\frac{\sinh[a_4/2]}{\operatorname{cn}(x\cosh[a_4/2], \frac{1}{\cosh[a_4/2]})}\right];$$
(2.1.1c)

$$\phi_{IV}(x) = -a_2 x + a_3; \tag{2.1.1d}$$

$$\phi_V(x) = 2\log\left[\frac{1+a_1\exp[-x+d/2+h]}{1-a_1\exp[-x+d/2+h]}\right],$$
(2.1.1e)

where we now have 4 unknown constants: a_1, a_2, a_3 and a_4 . Note that $a_4 = \phi_m$, the potential at the midplane of our system. By applying the appropriate bound-

ary conditions, these separate solutions can be combined to find the solution of the electrostatic potential for the entire system. At each interface we can write down two boundary conditions. Because of the mirror symmetry of our system, we can suffice with using the boundary conditions at x = d/2 and x = d/2 + h, the two interfaces of the right membrane. The first two boundary conditions are easily written down, they follow from the fact that the potential needs to be continuous at the interfaces. A second set of boundary conditions can be obtained by using Gauss's law.

Consider for example a Gaussian box S around the interface at x = d/2. Because our system is symmetric in the plane of the interfaces, we find in SI units

$$\oint_{dS} \mathbf{D}.d\mathbf{S} = \oint_{dS} \epsilon_r \epsilon_0 \mathbf{E}.d\mathbf{S} = A\sigma_e, \qquad (2.1.2)$$

where A is defined as the surface of the Gaussian box in the plane of the interfaces and where the dielectric constant of both the internal region of the membranes as well as our solvent is taken to be ϵ_r . We still think of our system as extending to infinity in the lateral directions, it therefore becomes a one-dimensional problem

$$-A\epsilon_r\epsilon_0 E(z=D/2-\delta) + A\epsilon_r\epsilon_0 E(z=D/2+\delta) = A\sigma_e, \qquad (2.1.3)$$

where δ is half the thickness of the Gaussian box and tends to zero. This then becomes

$$\frac{d\phi}{dx}(x=d/2-\delta) - \frac{d\phi}{dx}(x=d/2+\delta) = \frac{e\lambda_D\sigma_e}{k_B T\epsilon_r\epsilon_0} = 4\pi\lambda\tilde{\sigma},$$
(2.1.4)

where we have made the transition to our dimensionless variables ϕ, x, λ and $\tilde{\sigma}$ once again. A similar procedure gives the boundary condition at x = d/2 + h, so we finally have the following system of four boundary conditions

$$\phi_{III}(x = \frac{d}{2} - \delta) = \phi_{IV}(x = \frac{d}{2} + \delta);$$
 (2.1.5a)

$$\phi_{IV}(x = \frac{d}{2} + h - \delta) = \phi_V(x = \frac{d}{2} + h + \delta);$$
 (2.1.5b)

$$\phi'_{III}(x = \frac{d}{2} - \delta) - \phi'_{IV}(x = \frac{d}{2} + \delta) = 4\pi\lambda\tilde{\sigma}_m\alpha_3; \qquad (2.1.5c)$$

$$\phi'_{IV}(x = \frac{d}{2} + h - \delta) - \phi'_V(x = \frac{d}{2} + h + \delta) = 4\pi\lambda\tilde{\sigma}_m\alpha_4.$$
 (2.1.5d)

We have defined the surface charges as: $\tilde{\sigma}_i = \tilde{\sigma}_m \alpha_i$, with i = 1, 2, 3, 4 labeling the four interfaces from left to right, and where $\alpha_i = 1/(1 + r \exp \phi_i])$. Because of symmetry $\alpha_1 = \alpha_4 \equiv \alpha_{out}$ and $\alpha_2 = \alpha_3 \equiv \alpha_{in}$, where 'in' and 'out' refer to the inner and outer surfaces respectively. Applying the boundary conditions in (2.1.5) to the set of solutions in (2.1.1) gives us a system of 4 equations with 4 unknowns a_1, a_2, a_3, a_4 . By solving it, we find the total solution for the electrostatic potential in all regions.

At this point we would like to emphasise the difference of the second set of boundary conditions in (2.1.5) with respect to the second boundary condition used in Section 1.5. Here we see that the difference of the first derivatives of the potential (the electric field) on either side of the interface is proportional



Figure 2.2: The dimensionless electrostatic potential for membranes (full line) compared to plates of infinite thickness (dotted line) for charge regulation conditions. In going from top left to bottom right we have h = 20, d = 10 in (a), h = 3.0, d = 3.0 in (b), h = 0.5, d = 2.0 in (c) and finally h = 0.25, d = 1.0 in (d), where d and h are measured in units of Debye lengths: $d = D/\lambda_D$ and $h = H/\lambda_D$. The other parameters were set such that $\Sigma_m = 1.0$ and r = 1.0.

to the surface charge density. The boundary condition from Section 1.5 can be retrieved by assuming a vanishing electric field, or constant electrostatic potential, inside the membranes, as is typically done in DLVO theory. This will turn out to have an effect on the total charge of the "inner regio", consisting of the two surfaces at x = -d/2 and x = d/2, together with the solvent that resides between these two surfaces, as we shall demonstrate later on. First, we turn our attention to the electrostatic potential.

2.2 Electrostatic potential and ion densities

In Figure 2.2 the electrostatic potential is plotted for various membrane thicknesses and compared to the case where the membranes are of infinite thickness. In plot (a) we see that for a membrane thickness of 20 Debye lengths, the potential between the membranes is almost indistinguishable from that for plates of infinite thickness. As the membrane thickness (and plate separation distance) decreases we see the difference between the two setups increasing, with the potential between two membranes being increasingly lower than that between two infinite plates. Also, we can see that for the setup with membranes, the value of the electrostatic potential is higher at the inner surfaces than it is at the outer surfaces. We can note as well that for large membrane thickness, such as in (a) where the membrane is 20 Debye lengths thick, the potential profile becomes flat inside the membranes and therefore the electric field vanishes. It is therefore seen that the assumption of vanishing electric field inside the membranes, as made in standard DLVO theory, corresponds to taking the membranes to be very thick.

We can now also plot ion densities $\tilde{n}_{\pm}(x) \equiv n_{\pm}(x)/n_b$ in the inner and outer regions. This is done in Figure 2.3 for two different separation distances of d = 3.0 and d = 1.0. We see that when the membranes are far enough apart, the finite thickness of the membranes has no effect on the ionic density profile in the inner region. However, when the plates move closer together, the finite thickness effect of the membranes becomes more pronounced. In plot (b) it can be seen that, both for positive and negative ions, the deviation from the bulk density is smaller for the membranes, as compared to plates of infinite thickness. Remember that our surfaces are positively charged, the upper curves therefore correspond to negative ions, the lower curves to positive ions. We can also observe that the deviation from bulk density is lower at the outer surfaces than at the inner surfaces. This is to be expected, since as we saw in Figure 2.2, the potential is lower at the outer surfaces as well. Finally, we can see that within a few Debye lengths from the outer surfaces, the ion densities return to their bulk values, meaning they are no longer being influenced by the electric double layer at the surface.



Figure 2.3: The ion densities $\tilde{n}_{\pm}(x) \equiv n_{\pm}(x)/n_b$ in the inner and outer regions for two membranes of thickness h = 1.0, for separation distances d = 3.0 in (a) and d = 1.0 in (b). For comparison, the ion densities in the inner region are plotted for plates of infinite thickness, $h = \infty$. Remember that our surfaces are positively charged, the upper curves therefore correspond to anions, the lower curves to cations. The other parameters were set such that $\Sigma_m = 1.0$ and r = 1.0.

We have seen that, both for the electrostatic potential and the ion densities, a difference starts to occur between the inner and outer regions when the membranes get thinner and move closer together. It is also interesting to study what happens to the surface charge of the inner and outer surfaces. We have plotted, in Figure 2.4, the difference between surface charge on the inner and outer surfaces for several values of the membrane thickness h. Here, we have plotted the difference of the fractional charge between outer and inner surface, scaled to the outer surface charge: $\Delta \tilde{\alpha} \equiv (\alpha_{out} - \alpha_{in})/\alpha_{out}$ as a function of plate separation distance. Remember that α is the fraction of surface sites S that is actually protonated, it therefore takes values between 0 and 1. It can



Figure 2.4: Difference between the fractional surface charge for outer and inner surfaces, $\Delta \tilde{\alpha} \equiv (\alpha_{out} - \alpha_{in})/\alpha_{out}$ as a function of plate separation distance $d = D/\lambda_D$, for several values of the membrane thickness $h = H/\lambda_D$. Remember that α is the fraction of surface sites S that is actually protonated, it therefore takes values between 0 and 1. The other parameters were set such that $\Sigma_m = 1.0$ and r = 1.0.

be seen from the plot that the effect is larger for larger membrane thickness, as well as for smaller separation distance. This is not a surprising result. If we look, for example at the situation where h = 50, the thickness of the membranes causes the outer region not to be influenced by what is going on in the inner region. When the membranes move closer and closer together, the charge on the inner surfaces is expected to dissipate away, meaning $\alpha_{in} \to 0$, while on the outer surfaces the charge remains at its equilibrium value being described by α_{out} , like it would for a single double layer. The resulting effect is that $\Delta \tilde{\alpha} \to 1$ for vanishing separation distance, which is what we see in the plot. As the membranes get thinner, apparantly the outer surfaces are affected as well and surface charge is dissipated away, not only from the inner surfaces, but from the outer surfaces as well, resulting in a smaller value for $\Delta \tilde{\alpha}$.

We already mentioned the impact of the adjusted boundary conditions for finite thickness membranes on the total charge of the inner region. At this point, we want to calculate the total charge of the inner region, consisting of the two surfaces at x = -d/2 and x = d/2, together with the solvent in between. It is given, per surface area by

$$\Sigma^{tot} = \int_{-D/2}^{D/2} dz \left[\rho_+(z) - \rho_-(z) \right] + 2\sigma_e.$$
(2.2.1)

If we define a dimensionless total charge per surface area of λ_B^2 as $\Lambda \equiv \lambda_B^2 \Sigma^{tot}/e$

and use our dimensionless parameters, we find

$$\Lambda = \frac{-1}{4\pi\lambda} \int_{-d/2}^{d/2} dx \phi''(x) + 2\tilde{\sigma}_{in}.$$
(2.2.2)

By using the boundary conditions from (2.1.5), we find

$$\Lambda = \frac{-1}{4\pi\lambda} \left[4\pi\lambda\tilde{\sigma}_{in} + \phi'(x=d/2+\delta) + 4\pi\lambda\tilde{\sigma}_{in} - \phi \left(x=-d/2-\delta\right) \right] + 2\tilde{\sigma}_{in},$$
(2.2.3)

where $\tilde{\sigma}_{in}$ stands for the surface charge of the inner surfaces, $\tilde{\sigma}_{in} = \tilde{\sigma}_m \alpha_{in}$. This works out to

$$\Lambda = \frac{1}{4\pi\lambda} \left[\phi'(x = -d/2 - \delta) - \phi'(x = d/2 + \delta) \right].$$
(2.2.4)

From the expressions in (2.1.1), we see that the derivatives of the electrostatic potential are simply given by a_2 and $-a_2$ respectively, since we are considering mirror symmetry. Therefore, we finally find for the dimensionless total charge of the inner region

$$\Lambda = \frac{1}{4\pi\lambda}(2a_2) = \frac{a_2}{2\pi\lambda}.$$
(2.2.5)

Clearly, in our case where we assume mirror symmetry around x = 0, the expression for Λ is only zero if the electric field is zero inside the membranes. Remember that, in this expression, a_2 is directly proportional to the electric field inside the membranes. As can be seen from Figure 2.2, the electric field inside the membranes only vanishes if the membrane thickness is much larger than the Debye length. As the membrane thickness and separation distance decrease, as in plots (b), (c) and (d), we find a non-vanishing electric field inside the membranes. In these cases therefore, the inner region is not charge neutral. Our total system of course still needs to conform to charge neutrality. Therefore, we must conclude that for decreasing membrane thickness and separation distance, charge migrates from the inner region to the outer regions. We can plot the total charge in the inner region as a function of separation distance d, this is done in Figure 2.5 for various values of the membrane thickness h, and charge regulation parameter r.

We find that for large plate separations the inner region is indeed charge neutral in all cases. This is to be expected, as there is no interaction between the double layers. As separation distance decreases however, the total charge of the inner region increases and is always positive. Since our surfaces are positively charged, this means that counterions migrate from the inner region to the outer region, such that they no longer compensate the charge present on the surfaces. In plot (a) we have set r = 0, meaning that the surface charge is fixed on all four surfaces. We see that a thicker membrane has the effect of decreasing the charge migration. Apparently, as the membranes get thicker it is harder for the ions to migrate to the regions beyond the membranes. For a membrane thickness of h = 50, the effect is almost negligible. However, if we plug in a non-zero value for r, an additional proces will occur due to the charge regulation effect. In addition to ions migrating from the inner to the



Figure 2.5: The dimensionless total charge in the inner region $\Lambda \equiv \lambda_B^2 \Sigma^{tot}/e$ as a function of membrane separation distance $d = D/\lambda_D$. In all cases $\Sigma_m = 4\pi\lambda\tilde{\sigma}_m$ is set to 1.0, while the surface reaction constant is set to 0, 0.1 and 1.0 for plots (a), (b) and (c) repsectively.

outer regions, the surface charge will also migrate from the inner to the outer surfaces, as was seen in Figure 2.4. Still, we see in plots (b) and (c), that the total charge in the inner region increases for decreasing separation distance. We can therefore conclude that the ion migration process has a stronger effect than the surface charge migration.

From Figures 2.2, 2.3, 2.4 and 2.5, we can conclude that the finite thickness of the membranes has a profound effect on the behaviour of our system. As we have seen, electrostatic potential, ion density profiles as well as surface charges and the total charge in the inner region are all affected by the finite thickness of the membranes. We therefore expect that the interaction between objects is affected as well. To find out to what extent this is indeed the case, in the next section we look at the so-called disjoining pressure between double layers, taking into consideration the finite thickness of the membranes.

2.3 Langmuir's disjoining pressure

If we want to make predictions about the physical behaviour of our system, we need to know how the particles interact. That is, we want to try and find either the potential energy of interaction, or the force between the objects. We now turn our attention to the latter, by looking at the so-called disjoining pressure, which is defined as the force per unit area that one charged surface exerts on the other. Of course, once the force between the plates is known, the interaction energy can be obtained by integration, as shown in Appendix C.1. However, the disjoining pressure is interesting in itself, as it tells us about the force between the particles.

Suppose our solvent reservoir contains both positive and negative ions with number density n_b , such that the total ion density equals $2n_b$. The osmotic pressure of the reservoir is then given by $2n_bk_BT$. Our derivation for the dis-

joining pressure, denoted by Π , is inspired by [16]. We start by considering the total ion density in the region between the plates

$$n(x) = n_{+}(x) + n_{-}(x) = n_{b} \exp[-\phi(x)] + n_{b} \exp[\phi(x)] = 2n_{b} \cosh[\phi(x)].$$
(2.3.1)

The excess amount of ions between the plates with respect to the reservoir is then

$$\Delta n(x) = 2n_b \cosh[\phi(x)] - 2n_b = 2n_b (\cosh[\phi(x)] - 1) \ge 0 \quad \forall \phi(x). \quad (2.3.2)$$

So we see that in the space between the plates there will always be a higher ion density, as compared to the reservoir. This increased ion density builds up an excess pressure which drives the plates apart. This osmotic pressure is however counteracted by the Maxwell stress, which is a negative pressure due to the electric field between the surfaces. The net pressure, due to the osmotic pressure and the Maxwell stresses, must be the same for all x between the plates since we are considering our system to be in equilibrium. It is therefore most convenient to calculate it at the midplane between the plates (x = 0) where the electric field, and therefore the Maxwell stresses, are zero. This gives us the following expression for the disjoining pressure

$$\Pi(d) = k_B T \Delta n(x=0) = 2k_B T n_b (\cosh[\phi_m(d)] - 1), \qquad (2.3.3)$$

where $\phi_m(d)$ is the potential at the midplane $\phi_m(d) = \phi(x = 0; d)$ and where we have explicitly included the dependence on plate separation distance d in the equation. This expression for the disjoining pressure is known as Langmuir's equation. Note that (2.3.3) implies that the force between the plates is determined completely by the potential at the midplane ϕ_m . It is convenient to introduce a dimensionless disjoining pressure, given by

$$\tilde{\Pi}(d) \equiv \frac{\Pi(d)}{k_B T n_b} = 2(\cosh[\phi_m(d)] - 1).$$
(2.3.4)

To calculate the disjoining pressure, all we need is an expression for ϕ_m , the potential midway between the plates, which can easily be obtained from the various expressions for $\phi(x)$ we found earlier. In the next section, we first compare the disjoining pressure for two plates of infinite thickness, distinguishing fixed charge, fixed potential and charge regulation surface conditions. After that, we look at the impact of finite thickness by considering two parallel membranes. Note that, as an alternative method [17] the disjoining pressure can also be derived from the grand potential. It can be obtained by taking the derivative of the grand potential with respect to plate separation distance. We do not pursue this derivation in this report.

2.3.1 Disjoining pressure for plates of infinite thickness

Here, we consider again the setup as in Figure 1.3. In order to calculate the disjoining pressure for fixed charge (FC), fixed potential (FP) and charge regulation (CR) surface conditions, all we need is the potential at the midplane where $\phi_m = \phi(x = 0)$, and insert it into the equation for the disjoining pressure

$$\Pi(d) = 2(\cosh[\phi_m] - 1). \tag{2.3.5}$$

We use the expression from nonlinear Poisson-Boltzmann theory, which for charge regulation conditions was found in Chapter 1. From this expression, the equation for fixed surface charge is easily obtained, simply by setting the surface reaction constant to zero, r = 0. This corresponds to the situation where $\alpha = 1$, meaning all surface sites S are protonated. The expression for fixed surface potential conditions is given in Appendix A.6.1. In Figure 2.6 we have plotted the dimensionless disjoining pressure as a function of separation distance, for two parallel plates of infinite thickness. In the inset is the same plot, but this time on a log-log scale. For this plot we have set our parameters such that for large plate separation d, the disjoining pressure is equal for all three cases.



Figure 2.6: The reduced disjoining pressure $\Pi = \beta \Pi / n_b$ between two semiinfinite plates as a function of separation distance d for fixed surface charge (FC), fixed surface potential (FP) and charge regulation (CR) surface conditions. For this plot, the parameters were adjusted in such a way that the disjoining pressure approaches the same value for large d, in all three cases. This means $\Sigma = 1.0$ for the FC case, $\phi_s = 1.0$ for the FP case and $\Sigma_m = 3.72$ and r = 1.0 for the CR case. In the inset is the same plot, this time on a log-log scale.

Some remarkable observations can be made from these plots. There seems to be very different behaviour between fixed charge and charge regulation conditions on the one hand, and fixed potential conditions on the other. For fixed potential conditions the disjoining pressure levels off at a certain value for small plate separations, while for fixed charge and charge regulation conditions the disjoining pressure seems to diverge when the plates move closer together. Both for fixed charge and fixed potential conditions this seems to agree with what one would expect intuitively: On the one hand, for fixed potential, the surface charge can adjust itself through the adsorption and dissociation of ions. For fixed charge such that the disjoining force increases rapidly for decreasing plate separation distance. Therefore it seems plausible that the disjoining pressure would diverge.

For CR conditions we see that the curve lies right in between the FC and FP curves: $\Pi^{FP} \leq \Pi^{CR} \leq \Pi^{FC}$. Also, the disjoining pressure diverges for decreasing plate separation, albeit somewhat less strongly than for FC conditions. This behaviour is not very easy to understand. Under CR conditions, the surface potential and the surface charge can adjust themselves interdependently to changing conditions, such as plate separation distance. Naively, one would expect that as the plates move closer and closer together, the repulsive nature of the interaction between the charges on the surfaces would cause them to be dissociated from the surface and move beyond the inner region between the two plates. This process could potentially continue until all counterions have dissipated away at zero plate separation. The disjoining force then would not diverge. But this is apprarently not what happens: Some charges remain adsorbed on the surface. Necessarily some counterions will remain behind in the region between the plates to neutralize the surface charge. These remaining counterions are responsible for the diverging disjoining pressure.

From the log-log plot in the inset of Figure 2.6, we can make an estimate of the scaling behaviour of the disjoining pressure, as a function of plate separation. We find that $\tilde{\Pi}^{FC} \sim d^{-1}$ and $\tilde{\Pi}^{CR} \sim d^{-1/2}$, while $\tilde{\Pi}^{FP}$ tends to a constant for small d. This determination is however not exact. To that end, we would have to further analyse the expressions for the disjoining pressure, which we have not done for this report. However, our results seem to agree very well with what is found in the literature, e.g. [13]. This distinct behaviour for small separation distance of CR, as compared to FC and FP conditions warrants the statement that charge regulation surface conditions cannot be described as a limiting case of either FC or FP conditions. Rather, charge regulation conditions can be considered as a third boundary condition with its own unique dependence on plate separation distance.

The particular behaviour of the disjoining pressure under charge regulation conditions has, as an additional parameter, the surface reaction constant which we labeled r. It decribes the adsorption of, in our case, positive hydrogen ions, to surface sites S. As was shown in Section 1.3, it is related to the binding energy of the surface sites F_b . It is therefore interesting to look at the disjoining pressure under charge regulation conditions for varying r. We have done so in Figure 2.7. We have plotted the disjoining pressure on a log-log plot for values of r ranging from r = 0.1 to r = 50. For comparison, the plot for r = 0, which corresponds to fixed surface charge conditions is also shown. The scaling behaviour does not seem to depend strongly on the value of r. The curves for which $r \neq 0$ are all seen to have roughly the same slope for a certain value of d. The curve for FC conditions (r = 0) deviates considerably from this behaviour. As mentioned before, these observations are not very rigorous. To make more accurate claims about the scaling behaviour of the disjoining pressure, the expressions would have to be studied more thoroughly. We did not do so for this report.

It might also be interesting to look at how the surface charge behaves for vanishing plate separation. It is plotted for all three surface conditions in Figure 2.8. As for Figure 2.6, the parameters of our system are adjusted in such a way that at large plate separations the dimensionless surface charge $\tilde{\sigma}$ is the same for all three surface conditions, namely $1/4\pi$. Again, we see that the curve for CR conditions lies in between the curves for FC and FP conditions. As expected, the charge is dissipated from the surfaces for both the FP and CR



Figure 2.7: The disjoining pressure for charge regulation conditions, for varying values of the surface reaction constant r on a log-log plot. The case r = 0 corresponds to fixed surface charge conditions. We set $\Sigma_m = 1.0$ for this plot.



Figure 2.8: Surface charge $\tilde{\sigma} = \lambda_B^2 \sigma$ as a function of plate separation d for three cases: Fixed surface charge (FC), fixed surface potential (FP) and charge regulation (CR). For this plot we have set our parameters such that for large plate separation d, the surface charge $\tilde{\sigma}$ is equal for all three cases. This means $\Sigma = 1.0$ for the FC case, $\phi_s = 1.0$ for the FP case and $\Sigma_m = 3.72$ for the CR case. The surface reaction constant was set at r = 1.0 for the charge regulation case.

surface conditions as the plates move closer together, but more quickly for the FP case. In fact, the CR curve is so steep near d = 0 that even at very small plate separations there is still some surface charge left. This would seem to agree with the diverging disjoining pressure we observed earlier for CR conditions.

At this point however, we should note that the mean-field theory we are using loses its validity for extremely small plate separations. Since ions are treated as point-particles, their density between the plates can remain large, even for extremely small plate separation distances. This is of course not a physically realistic situation. Reasonably therefore, we should consider a cutoff distance, e.g. given by the ionic diameter. For values smaller than this cutoff distance, we consider our theory to no longer be valid. In Chapter 4 we will look at this in more detail when we look at the specific case of graphene and chlorosulfonic acid.

2.3.2 Disjoining pressure for membranes

We have already seen that the electrostatic potential, ion densities and surface charges are profoundly affected by the finite thickness of the membranes, as was shown in Figures 2.2, 2.3 and 2.4. Therefore, we expect a significant effect on the disjoining pressure as well. As before, once the potential is known, it is an easy task to find the disjoining pressure from (2.3.4). In Figure 2.9, we have plotted the reduced disjoining pressure for several values of the membrane thickness h under charge regulation conditions. For comparison, we have included the case for plates of infinite thickness $h = \infty$, which corresponds to the disjoining pressure we found in the previous section. In the inset is the same plot, this time on a log-log scale.



Figure 2.9: The reduced disjoining pressure as a function of separation distance under charge regulation conditions for several values of the membrane thickness. In the inset is the same plot, but this time on a log-log scale. The parameters were chosen such that $\Sigma_m = 1.0$ and r = 1.0.

From the plot, it is seen that the finite thickness of the membranes has
the effect of reducing the disjoining pressure between the objects considerably. Remember that, as was shown in Figure 2.5, in the case of membranes, the inner region is no longer restricted to the charge neutrality condition, as we had for plates of infinite thickness. However, the entire system, including the outer regions is still considered to be charge neutral. This means that ions, from the inner region, are able to migrate to the outer region. Since it is the excess ions in the inner region that are responsible for the disjoining pressure, this explains why the disjoining pressure is so much lower for membranes of finite thickness. When the membranes are very thick, the charge migration from inner to outer region will be more prohibited. This consideration makes the behaviour of the disjoining pressure for various values of the membrane thickness, as presented in Figure 2.9 understandable.

Also, we can see that for small membrane thickness, as wel as small plate separation distance, the curves in the log-log plot start to level off for vanishing plate separation d, implying the behaviour is no longer divergent, but showing behaviour that much more resembles the fixed surface potential case we saw earlier. As noted before however, we have to be careful when analysing behaviour at these extremely small separation distances, because at some point our mean field theory will no longer be able to provide valid results. We provide a more extensive analysis in Chapter 4.

Chapter 3

Image charges, Van der Waals forces and Zero Field

In this chapter, three different subjects are studied. As mentioned in the introduction, to complete our theory, we have to consider two final ingredients: The image charge effect and the well-known Van der Waals forces. We start out by considering the image charge effect. We investigate two separate methods of describing the image charge effect, in an attempt to determine to what extent this phenomenon affects our system and the strength of the interactions between the membranes. In the first method, we use the model of Chapter 2 to study membranes of finite thickness. However, this time we take the mismatch of the dielectric constants between object and solvent into account by adjusting the boundary conditions. In the second method we consider a modified Poisson-Boltzmann equation by introducting a correction potential.

Next, we turn to Van der Waals interactions between membranes of finite thickness. We use the standard expressions for the Van der Waals free energy of interaction from the literature, to obtain the Van der Waals disjoining pressure. We also study its dependence on membrane thickness. Finally, in the last section we take a small detour to study the so-called zero field solution. We demonstrate that, despite its straightforward computations, it has a high degree of accuracy for small plate separations and, under these circumstances, is a valid alternative to solving the Poisson-Boltzmann equation.

3.1 The image charge effect

3.1.1 The general theory

Objects, such as colloids, usually have a much lower dielectric constant than the solvent in which they are immersed. This is, for example true for biological systems in general, and certainly applies to our setup of graphene ($\epsilon_r \approx 7$) in chlorosulfonic acid ($\epsilon_r \approx 60$) as well. This mismatch in dielectric constants causes polarization charges to form on the interfaces. The effect these polarization charges have on the system can be represented by so-called image charges.

Imagine the situation as in Figure 3.1, where a charge q is placed between two interfaces, separated by a distance d. The dielectric constant in the inner region

is given by $\epsilon_{solvent}$, while the dielectric constant of the objects is denoted as ϵ_{object} . This setup is therefore representative of our model of two parallel plates. According to the general theory [18], every charge q causes an image charge to



Figure 3.1: Every charge in a solvent causes the appearance of an image charge accross a surface with a medium of different dielectric constant. Every image charge, in turn brings about a new image charge and so on. The prefactor Δ is a function that depends on the dielectric constants of both solvent and medium.

appear at its mirror point across the interfaces. This mirror charge then causes another mirror charge to appear and so on. Every time a charge is 'mirrored', its value is multiplied by a prefactor Δ , which is determined according to

$$\Delta = \frac{\epsilon_{solvent} - \epsilon_{object}}{\epsilon_{solvent} + \epsilon_{object}}.$$
(3.1.1)

From this formula, it is easily seen that the original charge and its image charge have equal sign if $\epsilon_{solvent} > \epsilon_{object}$, while the image charge has opposite sign if $\epsilon_{solvent} < \epsilon_{object}$. If the dielectric constants are equal, we find that $\Delta = 0$ and therefore the image charge effect will be nonexistent. If the image charge is of the same sign as the original charge, the original charge will be repelled by its own image charge. If on the other hand, the image charge is of opposite sign, an attractive interaction will be present. From this quick analysis we can therefore conclude that charges in a solvent are repelled from surfaces with a lower dielectric constant, while they are attracted to surfaces with a higher dielectric constant.

In general, as well as in our case of graphene in chlorosulfonic acid, the solvent has the higher dielectric constant, meaning the free ions in the solvent will be repelled from the surface. We therefore expect the ionic density profiles to drop near the surfaces.

To study the image charge effect, we apply two different methods. The first method is from [15] and consists of solving the system of equations for two membranes of finite thickness, as we did earlier in Chapter 2. However, this time the mismatch of dielectric constants between the solvent and the object is taken into account. This is done by adjusting the boundary conditions at the interfaces. In the second method by [19] we consider a modified Poisson-Boltzmann (mPB) theory that accounts for the image charge effect.

3.1.2 A system of membranes with index-mismatched conditions

As mentioned, our first method to study the image charge effect consists of solving our model for interacting membranes of finite thickness from Chapter 2, but this time with modified boundary conditions. We consider a system, identical to that of Section 2.1, with two membranes of finite thickness, immersed in a solvent that is connected to a reservoir. The solutions for the various regions of the system are again as given in (2.1.1).

$$\phi_I(x) = 2\log\left[\frac{1+a_1\exp[x+d/2+h]}{1-a_1\exp[x+d/2+h]}\right];$$
(3.1.2a)

$$\phi_{II}(x) = a_2 x + a_3; \tag{3.1.2b}$$

$$\phi_{III}(x) = 2 \operatorname{arcsinh} \left[\frac{\sinh[a_4/2]}{\operatorname{cn}(x \cosh[a_4/2], \frac{1}{\cosh[a_4/2]})} \right];$$
(3.1.2c)

$$\phi_{IV}(x) = -a_2 x + a_3; \tag{3.1.2d}$$

$$\phi_V(x) = 2\log\left[\frac{1+a_1\exp[-x+d/2+h]}{1-a_1\exp[-x+d/2+h]}\right].$$
(3.1.2e)

However, the boundary conditions need to be modified to include the dielectric constant mismatch between the object and the solvent. They now take the following form

$$\phi_{III}(x = \frac{d}{2} - \delta) = \phi_{IV}(x = \frac{d}{2} + \delta); \quad (3.1.3a)$$

$$\phi_{IV}(x = \frac{d}{2} + h - \delta) = \phi_V(x = \frac{d}{2} + h + \delta); \quad (3.1.3b)$$

$$\phi'_{III}(x = \frac{d}{2} - \delta) - \gamma \phi'_{IV}(x = \frac{d}{2} + \delta) = 4\pi \lambda \tilde{\sigma}_m \alpha_3; \qquad (3.1.3c)$$

$$\phi'_{IV}(x = \frac{d}{2} + h - \delta) - \gamma \phi'_V(x = \frac{d}{2} + h + \delta) = 4\pi \lambda \tilde{\sigma}_m \alpha_4, \qquad (3.1.3d)$$

where we have defined $\gamma \equiv \epsilon_{object}/\epsilon_{solvent}$. The factors of γ in (3.1.3) come about when the boundary conditions are derived using Gauss's law for two media with different dielectric constants, as we shall now demonstrate.

Consider, as in Section 2.1 a Gaussian box S around the interface at x = d/2. We can write

$$\oint_{dS} \mathbf{D}.d\mathbf{S} = A\sigma_e,\tag{3.1.4}$$

where A is the surface area of the Gaussian box in the plane of the interfaces. We still think of our system as extending to infinity in the lateral directions, it therefore becomes a one-dimensional problem

$$-A\epsilon_{sol}\epsilon_0 E(z=D/2-\delta) + A\epsilon_{obj}\epsilon_0 E(z=D/2+\delta) = A\sigma_e, \qquad (3.1.5)$$

where δ is half the thickness of the Gaussian box and tends to zero, and where we have abbreviated $\epsilon_{solvent}$ and ϵ_{object} to ϵ_{sol} and ϵ_{obj} respectively. When rewritten to our usual dimensionless variables, it becomes

$$\frac{d\phi}{dx}(x=d/2-\delta) - \frac{\epsilon_{obj}}{\epsilon_{sol}}\frac{d\phi}{dx}(x=d/2+\delta) = \frac{e\lambda_D\sigma_e}{k_BT\epsilon_{sol}\epsilon_0} = 4\pi\lambda\tilde{\sigma},\qquad(3.1.6)$$

with our dimensionless variable λ still defined as $\lambda = \lambda_D / \lambda_B$ and where λ_D and λ_B are the Debye length and Bjerrum length of the solvent, respectively. A similar procedure gives the boundary condition at x = d/2 + h, leading to the total set of boundary conditions given in (3.1.3).

By combining the expressions in (3.1.2) and (3.1.3), it is then quite straightforward to find the solutions for the potential, ion densities and disjoining pressure, as we did in Section 2.1. In Figure 3.2, we have plotted the dimensionless potential $\phi(x)$ for decreasing plate separation distance, both for the indexmatched as the index mis-matched case. We can also compare the disjoining



Figure 3.2: The dimensionless electrostatic potential for membranes for indexmatched case (blue curve), compared to index mis-matched case (green curve) under charge regulation conditions. For the index mis-matched case, $\gamma = \epsilon_{object}/\epsilon_{solvent} = 0.05$, meaning the dielectric constant of the solvent is much larger than that of the object. In going from top left to bottom right we have h = 20, d = 10 in (a), h = 3.0, d = 3.0 in (b), h = 0.5, d = 2.0 in (c) and finally h = 0.25, d = 1.0 in (d). The other parameters were set such that $\Sigma_m = 1.0$ and r = 1.0.

pressure for varying values of the dielectric constants. We have done so in Figures 3.3 and 3.4. From the plots in Figures 3.2, 3.3 and 3.4 we can make some interesting observations. First of all, when the plates have considerable thickness, the difference in dielectric constants does not seem to have much impact on potential and disjoining pressure. We can see this in plot (a) of Figure 3.2, where both curves fall right on top of each other, and in the right most plot of



Figure 3.3: The reduced disjoining pressure for various values of γ and membrane thickness h, as a function of plate separation distance d. From left to right, membrane thickness increases from h = 1.0 to h = 50.



Figure 3.4: The reduced disjoining pressure for various values of γ and membrane thickness h, as a function of plate separation distance d. From left to right, γ increases from $\gamma = 0.1$ to $\gamma = 10$.

3.3, where there is also very little difference between the three curves. Another remarkable observation comes from the left most plot of Figure 3.4, where it can be observed that for small values of γ the impact of finite thickness is minimal. We find these results surprising. In Section 3.1.1 we showed that, when an object has a lower dielectric constant than the solvent in which it is immersed, we expect a repulsive force as a result of the image charge effect. We therefore expect the ion densities to be lower close to the interface. We have plotted the ion densities in Figure 3.5 and clearly this is not what we observe in the plots. In plot (a) no image charge effect is observed at all, even for a significant discrepancy between the two dielectric constants. In fact, the only parameter that has significant impact seems to be the plate separation distance d. When this becomes small, we can see that the density of anions (Figure 3.5 (b)), as well as the potential in the inner region (Figure 3.2, (c) and (d)) increase. As a direct result, in Figure 3.3, we see that the disjoining pressure is larger for



Figure 3.5: The ion densities $\tilde{n}_{\pm}(x) \equiv n_{\pm}(x)/n_b$ in the inner and outer regions for two membranes of thickness h = 1.0, for index-matched and index mismatched conditions. The blue curve represents the index-matched condition, the green curve corresponds to the situation where the object has much lower dielectric constant, as compared to the solvent. In (a) separation distance is d = 3.0 and in (b) d = 1.0. Remember that our surfaces are positively charged, the upper curves therefore correspond to anions, the lower curves to cations. The other parameters were set such that $\Sigma_m = 1.0$ and r = 1.0.

smaller values of γ as well.

At this point, we are not convinced the method used in this section describes the image charge effect correctly. The main feature we would expect from the image charge effect is a drop in ion density close to the interfaces. This is not observed. We therefore now turn our attention to a different method for describing the image charge effect in the next section.

3.1.3 A modified Poisson-Boltzmann equation

The method described here is from Levin [19]. A modified Poisson-Boltzmann (mPB) equation is constructed that accounts for the ion-image and chargecharge correlation effect near the interfaces. This leads to an interaction potential W(z) that is essentially a correction to the general expression for the electrostatic potential. The full expression for this interaction potential W(z)is given in Appendix B.1.

The setup we consider is once again that of two parallel plates under charge regulation conditions, placed a distance D apart with a solvent filling the space between them, as in Figure 1.3. In the method by Levin it is assumed that the dielectric constant of the object is much lower than that of the solvent in which it is immersed: $\epsilon_{obj}/\epsilon_{sol} \ll 1$. This approximation is valid for the system we are considering, the applicable dielectric constants of graphene and chlorosulfonic acid being approximately 7 and 80 respectively. We elaborate further on this in Chapter 4.

Since for our setup the ion densities are relatively low, we choose to ignore the charge-charge correlation effect by setting the particle radius to zero, hereby considering the ions as point charges, as we have continuously done until now. This simplifies the expression for W(z), which now only describes the image charge effect. When written in SI units it takes the following form

$$W(z) = \frac{k_B T \lambda_B}{2} \int_0^\infty dk \frac{k}{p(\exp[2Dp] - 1)} \left\{ \exp[2pz] + \exp[2p(D - z)] \right\}.$$
(3.1.7)

In this expression z is the coordinate, D is the plate separation distance, λ_B is the Bjerrum length, $p = \sqrt{1/\lambda_D^2 + k^2}$ and k is a wave vector that comes about from the Fourier transform of the potential, which is used in the derivation. According to [19] the correction potential W(z) corresponds to the work necessary to insert an ion at position z and is calculated using the Güntelberg charging process. However, at this point we choose not to elaborate on the derivation of (3.1.7), but to simply apply it to our setup. By using the definition $\xi \equiv \lambda_D k$, along with our usual dimensionless variables, we can rewrite the equation

$$\beta W(x) = \frac{\nu^{\frac{1}{2}} \epsilon_{sol}^{-\frac{3}{2}}}{2} \int_{0}^{\infty} d\xi \frac{\xi}{\sqrt{1+\xi^{2}} (\exp[2\sqrt{1+\xi^{2}}d]-1)} \\ \times \left(\exp[2\sqrt{1+\xi^{2}}x] + \exp[2\sqrt{1+\xi^{2}}(d-x)] \right), \quad (3.1.8)$$

where we have multiplied W by β to find the dimensionless correction potential $\beta W(x)$, and have chosen to explicitly write the dielectric constant ϵ_{sol} in the expression. This means that we have also defined a new dimensionless variable, directly proportional to the ion bulk density $\nu \equiv (\beta^3 e^6/(8\pi^2 \epsilon_0^3))n_b$. This choice of variables is convenient because, at this point, we want to be able to vary ϵ_{sol} as one of our parameters. We have plotted the dimensionless correction potential $\beta W(x)$ for various value of the solvent dielectric constant in Figure 3.6. Immediately we see that the correction potential is smaller for larger values



Figure 3.6: The dimensionless correction potential $\hat{W}(x) \equiv \beta W(x)$, for various values of the solvent dielectric constant. The dimensionless ion bulk density was set at the best known value for CSA: $\nu = 492$, while plate separation distance was set to d = 4.

of the solvent dielectric constant. At first sight this might seem counterintuitive,

as one would expect the correction potential to be larger when the difference in dielectric constants of object and solvent is larger. We come back to this when we plot the corrected ion density profiles. Note that in this section, we have placed our left and right planar surfaces at x = 0 and x = d respectively.

At this point we want to mention that we have jumped a little ahead of ourselves and, in plotting Figure 3.6, we have used the best known values of the parameters for the graphene/CSA system. Since we want to determine whether the image charge effect has a large impact on our actual system, this seems like a sensible thing to do. Since βW must be seen as a correction to the dimensionless potential, we need to compare its values to that of the potential in the actual graphene/CSA system. As shown in Chapter 4, typical values for the dimensionless electrostatic potential near a surface are of the order of ~ 2 at a distance of one Debye length. We can therefore already see that βW is a small correction indeed, especially for larger values of the dielectric constant ϵ_r .

Once the correction potential $\beta W(x)$ is known, we use it to construct a modified Poisson-Boltzmann equation [19]. Together with the usual boundary conditions, this leads to the following boundary value problem

$$\hat{\phi}''(x) = \exp[-\beta W(x)] \sinh[\hat{\phi}(x)]; \qquad (3.1.9a)$$

$$\hat{\phi}'(x=d/2) = 0;$$
 (3.1.9b)

$$\hat{\phi}'(x=d) = 4\pi\nu^{-\frac{1}{2}}\epsilon_r^{-\frac{1}{2}}\zeta\alpha.$$
(3.1.9c)

Again, in order to be able to explicitly write the dielectric constant ϵ_r in our equations, we have defined a new dimensionless variable, $\zeta \equiv (\beta e^2/4\pi\epsilon_0)^2 \sigma_m$. It is a dimensionless surface charge density. Also, we have added a caret to the notation for the potential, $\hat{\phi}(x)$, in order to distinguish the solution of the modified Poisson Boltzmann equation from the standard Poisson Boltzmann equation. The set of equations in (3.1.9) can be solved numerically to find the 'corrected' electrostatic potential $\hat{\phi}(x)$. Once this is done, it is an easy task to compute the corrected ion density profiles

$$\hat{n}_{\pm}(x) \equiv \exp[-\beta W(x)] \times \exp[\mp \phi(x)]. \tag{3.1.10}$$

In Figure 3.7 we have plotted the ion densities for increasing values of the solvent dielectric constant ϵ_{sol} . To get some general idea of how the ioin densities behave under the influence of the correction potential W(x), we first plot them for the general values we have used until now. In Figure 3.6, we already saw that the correction term βW decreases, for increasing solvent dielectric constant. This trend continues in Figure 3.7, where we see that the corrected ion density profiles, represented by the green curves, are increasingly close to the uncorrected curves, as the dielectric constant increases, going from the left to the right plot. As mentioned earlier, at first sight this appears contrary to what one would expect. From simple considerations, one would expect the effect of image charges on the system to be larger when the difference in dielectric constants is larger. This is for example easily seen from the expression for Δ in (3.1.1). However, in the general theory of Section 3.1.1, the screening by the solvent is not taken into account. In fact, as the solvent dielectric constant increases, the screening of the ions, by the solvent increases as well. One could state that the screening effect causes the ions to not be able to 'see' its image charges.



Figure 3.7: The ion density profiles between two parallel plates for increasing values of the solvent dielectric constant. Going from left to right, the dielectric constant is set to 10, 30 and 60 respectively. The blue curves correspond to the uncorrected ion density profiles, without the correction term W, the green curves correspond to the corrected density profiles. For this plot we set the parameters such that $\nu = 1.0$ and $\zeta = 1/4\pi$, while plate separation distance was set to d = 4.

Of course, it is again prudent to plug in the values of our actual graphene/CSA system. Since the dimensionless electrostatic potential takes on values ~ 2 at a distance of one Debye length, and even higher values closer to the surface, the ion densities are expected to be relatively large. They are plotted in Figure 3.8 for the graphene CSA system. Again, we see that the difference between the



Figure 3.8: The ion density profiles between two parallel plates for increasing values of the solvent dielectric constant. Going from left to right, the dielectric constant is set to 10, 30 and 60 respectively. The blue curves correspond to the uncorrected ion density profiles, without the correction term W, the green curves correspond to the corrected density profiles. For this plot we set the parameters to the best known values for the graphene CSA system.

corrected and the uncorrected profiles gets smaller for increasing values of the solvent dielectric constant. In the middle and right most plot the two curves are

virtually indistinguishable. We then finally come to the conclusion that, for our setup of graphene in chlorosulfonic acid, with its large difference in dielectric constants, the image charge effect can considered to have a very small contribution. In Chapter 4 we apply the general theory of Chapter 2 to the specific case of graphene in chlorosulfonic acid. Considering the results found in this section, we think it is justified to not take the image charge effect into account. But first, in the next section, we want to look at the final ingredient of our theory, the Van der Waals forces.

3.2 Van der Waals disjoining pressure

It was already mentioned in the introduction that in DLVO theory, the total interaction between objects immersed in a solvent is a combination of double layer forces and Van der Waals forces. The double layer forces have been extensively studied in Chapter 2 and were shown to always be repulsive, for the cases we considered. Now, we turn our attention to Van der Waals forces. Van der Waals forces are relatively weak and very short-ranged attractive forces. However, they do play an important role in determining the overall interaction between atoms, molecules and surfaces.

Van der Waals forces, named after Dutch scientist Johannes Diderik van der Waals, are relatively weak forces between atoms or molecules and vanish quickly as the distance between the objects increases. Nevertheless, at short range they certainly cannot be ignored. Van der Waals forces generally contain a repulsive and an attractive contribution. The repulsive contribution occurs at extremely small separation distances and is a direct result of the Pauli exclusion principle. When two atoms get too close, their electron clouds will begin to overlap. We will not consider this contribution. The attractive Van der Waals forces result from either permanent, or instantaneously induced dipoles, the latter also being referred to as the London dispersion force [12].

In this section, we study Van der Waals forces between membranes of finite thickness. We consider therefore the setup as in Figure 2.1. From [20] we find the free energy of interaction, due to Van der Waals interaction for a setup with this specific geometry, per unit area to be given by

$$f = -\frac{A_H}{12\pi} \left[\frac{1}{D^2} - \frac{2}{(D+H)^2} + \frac{1}{(D+2H)^2} \right],$$
(3.2.1)

where A_H is the so called Hamaker constant, a materials constant that measures the relative strength of the Van der Waals forces and depends on the properties of the two objects and the intervening media. We shall come back to the Hamaker constant in the context of graphene dissolution in chlorosulfonic acid in more detail in Chapter 4. As before, D is the separation distance between the membranes and H is their thickness. The Van der Waals disjoining pressure can now be obtained by differentiating this expression

$$\Pi^{VdW} = -\frac{\partial f}{\partial D} = -\frac{A_H}{12\pi} \left[\frac{2}{D^3} - \frac{4}{(D+H)^3} + \frac{2}{(D+2H)^3} \right].$$
 (3.2.2)

If we define a dimensionless Hamaker constant as $\tilde{A}_H = A_H/k_B T$, we can write

the dimensionless Van der Waals disjoining pressure as

$$\tilde{\Pi}^{VdW} = -\frac{4\lambda \tilde{A}_H}{3} \left[\frac{1}{d^3} - \frac{2}{(d+h)^3} + \frac{1}{(d+2h)^3} \right],$$
(3.2.3)

where we have also returned to our dimensionless variables λ , d and h, which are defined as before, such that λ is a dimensionless parameter and d and h represent the dimensionless separation distance and membrane thickness respectively: $\lambda = \lambda_D / \lambda_B$, $d = D / \lambda_D$ and $h = H / \lambda_D$. The Van der Waals disjoining pressure is plotted in Figure 3.9 for various values of the Hamaker constant \tilde{A}_H and membrane thickness h. We see that the interaction is attractive in all



Figure 3.9: The reduced Van der Waals disjoining pressure between two parallel membranes as a function of plate separation distance $d = D/\lambda_D$ for various values of the membrane thickness $h = H/\lambda_D$. Note that the disjoining pressure is negative, meaning the interaction is attractive. For this plot the parameters were set such that $\lambda = 1.0$ and $\tilde{A}_H = 2.5$.

cases. From the left plot, we see that a larger Hamaker constant corresponds to stronger attraction. From the right plot, we can see that Van der Waals forces are generally weaker if the membranes are thinner. This makes sense, since if the membranes are thinner, there is 'less bulk material' available to produce the attractive force. Remember that Van der Waals forces are caused by (induced) dipole interactions.

We now have all the ingredients to look at our model of graphene in chlorosulfonic acid. In the final chapter, we start by looking at both graphene and chlorosulfonic acid in more detail. We talk about its general properties and especially its physical properties that determine the strength of both the Van der Waals interaction, and the interaction due to the electric double layers. After that, we calculate the total disjoining pressure for our system by looking at the combined effect of the Van der Waals and double layer disjoining pressures.

3.3 Zero field solution

At this point, we would like to make a small detour and present an alternative method for solving the two-plate problem, from that in Section 1.5. Although it does not produce any actual new results, we still want to include it in this report, as this method produces results that are in very good agreement with the full nonlinear Poisson-Boltzmann theory, while at the same time being very straightforward in its computations. It is called the zero field method and is due to [16] and [17]. All results in this section will be computed for the physically most interesting case of charge regulation surface conditions. We consider a setup of two parallel plates of infinite thickness, as in Figure 1.3.

The method of the zero field solution starts with an observation. In Figure 3.10, we have presented the dimensionless electrostatic potential for this particular setup for decreasing plate separation, from both the Debye-Hückel and the full nonlinear solution.



Figure 3.10: The dimensionless electrostatic potential between two double layers for various plate separations for the case of charge regulation from both Debye-Hückel and Poisson-Boltzmann theory. Plate separation runs from d = 4 in the top left figure, via d = 2 and d = 1, to d = 0.2 in the lower right figure and is measured in Debye lengths. For this plot the parameters are set such that $\Sigma_m = 1.0$ and the surface reaction constant r = 1.0.

Some important observations can be made from this figure. First, for decreasing plate separation the mean value of the potential between the plates increases. Second, for large separations the Debye-Hückel result agrees with full Poisson-Boltzmann theory, but as the plate separation decreases, the Debye-Hückel theory loses its validity. This happens at the threshold where the dimensionless potential is $\phi \approx 1$, and means that for larger values of ϕ we can no longer use Debye-Hückel theory and therefore need to resort to, in most cases numerical solutions of the Poisson-Boltzmann equation. These observations confirm what we saw in previous sections.

However, another interesting fact that is immediately clear upon looking at the plots is that, as the plate separation distance decreases, the potential profile becomes increasingly flat. A flat potential profile corresponds to a vanishing electric field. This means that, for interplate distances that are of the order of one Debye length, or less, we can consider the limit of a very weak, or zero electric field. By using the zero-field limit, the two-plate problem can be solved without the need for solving the Poisson-Boltzmann equation, as we now demonstrate.

If the potential profile is flat, obviously the potential is the same everywhere between the plates and at the surfaces. This value of the potential will be labeled as $\bar{\phi}$. As mentioned before, the power of the zero field solution stems from the fact that the Poisson-Boltzmann equation need not be solved to find it. Instead, $\bar{\phi}$ can be derived from the constraint of charge neutrality: The total charge from mobile ions between the plates balances the adsorbed charge on the plates. When written in SI units the constraint appears as

$$e \int_{-D/2}^{D/2} [n_{+}(z) - n_{-}(z)] dz + 2e\sigma_{m}\alpha = 0, \qquad (3.3.1)$$

where e is the elementary charge, D is the plate separation distance, n_{\pm} are the ion densities, σ_m is the maximum surface charge density with all sites on the surface charged and α denotes the fraction of sites that is actually charged, as before. This can be rewritten to our dimensionless units to become

$$\int_{-d/2}^{d/2} [\tilde{n}_{+}(x) - \tilde{n}_{-}(x)] dx = -16\pi\lambda \tilde{\sigma}_{m}\alpha.$$
(3.3.2)

The next observation is that, for a flat potential profile, the ion densities will also be independent of position between the plates and can be written as

$$\tilde{n}_{\pm}(x) = n_{\pm}(x)/n_b = \tilde{n}_{\pm} = \exp[\mp \bar{\phi}].$$
(3.3.3)

This makes the integral in (3.3.2) very straightforward to solve, such that we get

$$-2\sinh[\bar{\phi}]d = -16\pi\lambda\tilde{\sigma}_m\alpha. \tag{3.3.4}$$

Inversion then gives for the mean electrostatic potential between the plates

$$\bar{\phi} = \sinh^{-1} \left[\frac{8\pi \lambda \tilde{\sigma}_m}{d(1 + r \exp[\bar{\phi}])} \right], \qquad (3.3.5)$$

where \sinh^{-1} stands for the inverse of hyperbolic sine (not $1/\sinh$) and we have inserted our usual expression for α . This is again a self-consistent equation that can be solved for $\overline{\phi}$.

The derivation of the zero-field solution in (3.3.5) was very straightforward, especially compared to the method of solving the two-plate problem using the nonlinear Poisson-Boltzmann equation of Section 1.5. It is therefore interesting to find out how its results compare, and what its range of applicability is. One would expect the zero-field solution to be valid for small plate separation distances, or for circumstances where the Debye screening length is relatively large. In other words, whenever the distance between the plates is of order one Debye length or less, resulting in a flat potential profile as we saw in Figure 3.10. At this point we would therefore like to compare the disjoining pressure found from zero-field theory to that from Debye-Hückel and Poisson-Boltzmann theory. The disjoining pressure is easily determined from the electrostatic potential at the midplane ϕ_m . Obviously, in the zero-field case $\phi_m = \bar{\phi}$. The expression for the reduced disjoining pressure is

$$\tilde{\Pi}(d) \equiv \frac{\Pi(d)}{k_B T n_b} = 2(\cosh[\phi_m] - 1).$$
(3.3.6)

It is plotted in Figure 3.11 for all three solutions. It is immediately clear that the



Figure 3.11: The reduced disjoining pressure between two parallel plates as a function of plate separation. Plotted are the Debye-Hückel(DH), Poission-Boltzmann(PB) and Zero-field(ZF) solution. For this particular plot the paramaters were set such that $\Sigma_m \equiv 4\pi\lambda\tilde{\sigma}_m = 2.5$ and r = 1.0.

zero-field approach yields very good results for small plate separation distances, while Debye-Hückel theory is a good approximation for large plate separation distances. This is even more clearly seen in the log-log plot presented in the inset. In Figure 3.12 we have plotted the disjoining pressure for increasing values of Σ_m . When Σ_m is small, as in plot (a), we see that all three solutions produce similar results. However, with Σ_m increasing, the zero-field solution loses its validity for large plate separation distances, while the Debye-Hückel solution is no longer accurate at small plate separation distances. But surprisingly, the zero-field solution even produces good results under conditions when it is not expected to. For example, in Figure 3.10 (c), the potential profile shows significant curvature. However, the disjoining pressure from zero-field theory shows accurate results under these circumstances, as can be seen in Figure 3.12 (b), where the disjoining pressure is plotted for similar values of the parameters. Since the derivation of the solution for zero-field theory is based on the assumption that the surfaces are close together, resulting in a flat potential profile, this



Figure 3.12: The reduced disjoining pressure between two parallel plates as a function of plate separation distance, from Debye-Hückel (DH), Poisson-Boltzmann (PB) and zero-field (ZF) solutions with $\Sigma_m \equiv 4\pi\lambda\tilde{\sigma}_m$ set to 0.1, 1.0, 5.0 and 10 for plots (a), (b), (c) and (d) respectively. The surface reaction constant was set to r = 1.0.

result is surprising. We can therefore state that the zero field method has a higher degree of applicability than would be expected from first considerations.

The zero-field solution is not pursued any further in this report. However, the results in this section demonstrate that it is a viable approach for a system of graphene and chlorosulfonic acid, where the combination of a large Debye length for chlorosulfonic acid on the order of 20nm, and an interplate separation for graphene of approximately 0.3 nm, certainly fulfill the requirement of strongly overlapping double layers.

Chapter 4

Applying the theory to graphene and chlorosulfonic acid

In Chapter 2 we looked at the double layer interactions between two membranes of finite thickness under charge regulation conditions. In Chapter 3, we studied the Van der Waals interactions, also for membranes of finite thickness. Also in Chapter 3, we investigated the image charge effect and found that its impact on our system is not very significant, so we made the decision to ignore it. This means we now have all the ingredients to look at the total interaction between two membranes, immersed in an ionic solvent. Of paramount importance is the question of attraction versus repulsion: From DLVO theory we know that, when double layer and Van der Waals interactions are combined, in general one finds attraction at very small separation distances, followed by a repulsive peak at somewhat intermediate distance and finally a small secondary region of attraction, followed by vanishing interaction for large separation distances. We expect to find similar behaviour for our graphene/CSA system. Since we are especially interested in describing the spontaneous exfoliation of graphene layers in chlorosulfonic acid, we mostly want to know at what separation distance the threshold between attractive and repulsive interaction takes place.

In this chapter, we will determine the best known values of all parameters of interest, for the graphene/CSA system. That is, we want to find the appropriate values for the dielectric constants, the bulk ion density, the layer thickness of graphene etc. Once these values are determined, we can insert them into our general theory from the previous chapters and find the total interaction. We start by providing some additional information about graphene and chlorosulfonic acid in the next two sections. Then in Section 4.3, we put everything together and present the main result of this report. Finally in Section 4.4, we take a critical look at our model and review its limitations. We consider the simplifying assumptions made and discuss possible improvements.



Figure 4.1: Graphite can be considered to be built up of many layers of graphene, where the layers are stacked in such a way that atoms in one layer are placed at the hexagon centres of the layers above and beneath it.

4.1 About graphene

At this point we would like to provide some background information about graphene, and look at its physical characteristics. In the introduction we already discussed some of its properties, but now it is time to look in more detail. According to Geim [22], graphene is the thinnest material in the universe and the strongest ever measured. Graphene is capable of sustaining current densities six orders of magnitude higher than copper. It also boasts extremely high thermal conductivity and stiffness. According to Geim [22], graphene needs to be defined as "sufficiently isolated from its environment to be considered free-standin".

Graphene was first isolated in 2004 by Geim and Novosolev [1], using a method called mechanical cleavage. This method consists of repeatedly using adhesive tape on a sample of graphite, until a single layer of graphene is left. They were awarded the Nobel prize for their achievement in 2010. As mentioned in the Introduction, over the years several alternative production methods for graphene have been developed, but the resulting yield and quality of the graphene samples is often not satisfactory [7].

However, we are of course especially interested in the physical properties of graphene that affect its solubility. As is well known, graphene is an allotrope of carbon consisting of a single layer of graphene, arranged in a hexagonal lattice. Other allotropes of carbon include diamond and graphite, where diamond has a lattice crystalline structure and graphite can be considered to be built up of many layers of graphene, stacked on top of each other, where the stacking is such that there are atoms in the upper layer placed at the hexagon centres of the lower layer [23]. The thickness of a single layer of graphene is taken from [24] as 0.37 nm. In the process of exfoliation of graphite in chlorosulfonic acid, as described in [8], typically platelets of single layer graphene are formed with lateral dimensions of the order of 100nm. This makes our one-dimensional model, introduced in the previous chapters a valid description for the graphene/CSA system.

To find a value for the maximum charge density, σ_m of our graphene surfaces, we can simply consider the density of carbon atoms in graphene. In the hexagonal structure of graphene layers, the sides of the hexagon have dimen-

sion l = 0.142nm. By using the expression for the surface area of a hexagon $A = 3\sqrt{3}l^2/2$, we find the surface density of carbon atoms to be $\sigma_m = 3.82 \times 10^{19}$ m^{-2} . For convenience, we use the dimensionless surface charge density, defined earlier as $\zeta = (\beta e^2/4\pi\epsilon_0)^2 \sigma_m$, whose value is then given by $\zeta = 12.4 \times 10^4$.

In Section 3.1.3, we already mentioned that the appropriate value to use for the dielectric constant of graphene is ≈ 7 . Considering the metallic properties of graphene this may seem unexpected, one would potentially expect the appropriate dielectric constant to be infinite. However, we have to keep in mind that we actually need to consider the out-of-plane dielectric constant. The characteristic geometric properties of graphene, especially its extremely small thickness compared to its other dimensions, make it plausible that its properties depend on the specific orientation as well. Indeed, in [25] it is found that the out-of-plane dielectric constant of graphene has a value of approximately $\epsilon_r \approx 7$ and this is the value we will use in our model. Next, we take a closer look at the superacid called chlorosulfonic acid.

4.2 About Chlorosulfonic acid

Chlorosulfonic acid, also known as chlorosulfuric acid is what is known as a superacid, meaning it has an acidity greater than 100% sulfuric acid. It is a colourless liquid with chemical structure formula ClSO₃H and consists of tetrahedral molecules, as schematically drawn in Figure 4.2. Chlorosulfonic acid is a mineral acid with a Hammet acidity value of -12.78 [26] in its pure form. It has a relatively high dielectric constant given by $\epsilon_r \approx 60 \pm 10$ [10,11] at 15° C, but values of 100 are also reported.



Figure 4.2: A chlorosulfonic acid molecule is a tetrahedral molecule.

We make two assumptions about chlorosulfonic acid. The first is that it has the following autodissociation mode

$$ClSO_3H \Longrightarrow ClSO_3^- + H^+$$
 (4.2.1)

Paul and coworkers [27] concluded this to be the case, among other things, from the high electrical conductivity of solutions of potassium and sodium chlorosulfates in chlorosulfonic acid. Our solvent of pure chlorosulfonic acid therefore consists of neutral ClSO_3H molecules, along with ClSO_3^- and H^+ ions.

Now, to find a value for the bulk density of ions in pure chlorosulfonic acid, we need a value for its degree of autodissociation. This brings us to our second assumption, which entails that pure chlorosulfonic acid has a small degree of autodissociation. From [28] we have a value for the autodissociation constant of $10^{-8} \text{ (mol/kg)}^2$. For comparison, sulfuric acid has a degree of autodissociation of $10^{-4} \text{(mol/kg)}^2$, compared to for example water's $10^{-14} \text{(mol/kg)}^2$. Because the degree of autodissociation is relatively small, the concentration of neutral ClSO₃H molecules can be considered constant and we can calculate our bulk concentration of ions easily from the degree of autodissociation. By using the density of chlorosulfonic acid, which is quoted as 1.7410 g/cm³ [10], we can find a value for the number density of both species of ions. It is found to be given by $n_b = 1.056 \times 10^{23} \text{ m}^{-3}$. Again, for convenience we use our dimensionless bulk ion density, defined earlier as $\nu = (\beta^3 e^6 / 8\pi^2 \epsilon_0^3) n_b$, to find its value as $\nu = 492.3$. From these numbers, it is now straightforward to find values for the Bjerrum length and Debye length at room temperature, which are respectively given by $\lambda_B = 0.95 \text{ nm}$ and $\lambda_D = 19.9 \text{ nm}$.

There are several complicating factors to consider, for example the effect of autoprotolysis of chlorosulfonic acid. This means that instead of roaming free, the H^+ ions are bound to neutral chlorosulfonic acid molecules. The equilibrium than looks like

$$2 \operatorname{ClSO}_3 \operatorname{H} \Longrightarrow \operatorname{ClSO}_3^- + \operatorname{ClSO}_3 \operatorname{H}_2^+ \tag{4.2.2}$$

This would mean that, as an additional step, there is an equilibrium between surface sites S and the positively charged CSA molecule

$$S + ClSO_3H_2^+ \Longrightarrow SH^+ + ClSO_3H$$
 (4.2.3)

In their experiments, Matteo Pasquali and co-workers [8] also considered mixtures of chlorosulfonic acid with sulfuric acid H_2SO_4 to be able to control the level of acidity of their solvent. In this mixture, chlorosulfonic acid acts as a weak acid and the following equilibrium needs to be considered

$$ClSO_3H + H_2SO_4 \Longrightarrow ClSO_3^- + H_2SO_5^+$$

$$(4.2.4)$$

In this setup, the acid strength can be controlled by the ratio of chlorosulfonic acid to sulfuric acid: A higher concentration of chlorosulfonic acid leads to a stronger acid. We consider only the most simple case: pure chlorosulfonic acid with free roaming ClSO_3^- and H^+ ions.

We then have to consider the equilibrium between ${\rm H^+}$ ions and the surface sites S

$$S + H^+ \Longrightarrow SH^+$$
 (4.2.5)

Several models, due to [29], are available for describing this process. One could assume sites S that consist of a single carbon atom. This is the simplest model and would mean that every H^+ ion that is bound to the surface is bound to a single carbon atom. One could also envisage sites that are made up of several carbon atoms, where each adsorbed H^+ ion is in some way shared by and bonded with several carbon atoms. We will not do this here, but instead assume that a H^+ ion is always bonded to a single carbon atom.

4.3 Total disjoining pressure: Attraction vs repulsion

We start this section by summarizing, in Table 4.1, the best known values of the parameters for our system of graphene and chlorosulfonic acid. All values in

Physical property	SI units	Dimensionless units
dielectric constant CSA		$\epsilon_r = 60 \pm 10$
dielectric constant graphene		$\epsilon_r = 7$
bulk ion density CSA	$n_b = 1.056 \times 10^{23} m^{-3}$	$\nu = 492.3 \equiv \nu_0$
Bjerrum length CSA	$\lambda_B = 0.95$ nm	
Debye length CSA	$\lambda_D = 19.9$ nm	
layer thickness graphene	H = 0.37nm	h = 0.0186
maximum surface charge	$\sigma_m = 3.82 \times 10^{19} {\rm m}^{-2}$	$\zeta = 12.4 \times 10^4$
surface reaction constant		r = 0.02
Hamaker constant	$A_H = 1.0 \times 10^{-20} \text{J}$	$\tilde{A}_H = 2.5$

Table 4.1: Best known values for the graphene/CSA system at T = 293K

Table 4.1 were already mentioned in previous sections, except for the Hamaker constant A_H and the surface reaction constant r. The value for the dimensionless Hamaker constant of 2.5 is taken from [30] and is valid for a system of two graphene layers, acting across a region filled with water. We were unable to find values for a system of graphene and chlorosulfonic acid specifically in the literature. The value of the Hamaker constant does depend on the salinity (ion concentration) of the intervening media, but the dependence is weak [31]. Since water and chlorosulfonic acid have dielectric constants of roughly the same order of magnitude, the assumption that a value of $\tilde{A}_H \approx 2.5$ can also be used for the graphene/CSA systems seems justified.

The other quantity for which, as of yet, we have not determined a physical value is the surface reaction constant r. If we know a typical value for α , the fraction of surface sites that is protonated under typical circumstances, we can use the model for a single double layer under charge regulation conditions to adjust the parameter r in such a way as to obtain the desired value of α . In other words, we use r as a fitting parameter. We found, from unpublished exeperimental work generously provided by Robert Pinnick [29] that α typically ranges from 0.007 to 0.044. We will adopt the most basic model in which a single hydrogen ion bonds to a single carbon atom. The quoted values for α then simply imply that between 0.7 and 4.4% of the carbon atoms on the surface are protonated under typical circumstances in pure chlorosulfonic acid. As mentioned, we can use these values to find a value for our parameter r. In doing so, we find a value for the surface reaction constant of $r \approx 0.02$, which is what we shall use.

It is also interesting to look at typical values of the electric potential for our system. In Figure 4.3, we have plotted the electrostatic potential near a single electric double layer, for the values given in Table 4.1. At a distance of one Debye length from the surface, we see that the dimensionless potential attains a value of ≈ 2 , which increases to a value of the order ≈ 8 , very close to the



Figure 4.3: The dimensionless electrostatic potential $\phi = \beta e \psi$, near a single graphene platelet in chlorosulfonic acid as a function of distance, measured in units of Debye lengths. Parameter values were used from Table 4.1.

surface. These are quite large values for colloidal systems and from Section 1.4, we know that linear theory cannot be used if $\phi \gtrsim 1$. We expect the potential to be higher still for interacting objects, with overlapping double layers. Our choice for nonlinear theory is therefore shown to be justified.

Finally, we are now in a position to add all the ingredients of our theory together. We can find the total disjoining pressure by adding the contributions from the Van der Waals and the electric double layer forces

$$\tilde{\Pi}^{tot} = \tilde{\Pi}^{DL} + \tilde{\Pi}^{VdW} = 2(\cosh[\phi_m] - 1) - \frac{4\lambda\tilde{A}_H}{3} \left[\frac{1}{d^3} - \frac{2}{(d+h)^3} + \frac{1}{(d+2h)^3} \right]$$
(4.3.1)

In this expression, the potential at the midplane ϕ_m is determined from the theory in Chapter 2. Next, we insert all values of our parameters from Table 4.1, to find the total disjoining pressure for the graphene/CSA system. It is plotted in Figure 4.4. The upper dashed curve represents the repulsive interactions from the double layer forces, the lower dashed curve represents the attractive interactions from Van der Waals forces, while the blue curve represents their sum: the total disjoining pressure. It is seen that the disjoining pressure vanishes for large plate separation distance d, increases to reach maximum repulsion at a separation distance of around 0.25 Debye lengths, and then it quickly decreases and turns into an attractive interaction for smaller separation distances. Also this transition is very steep, meaning that for a small difference in separation distance, the interaction changes from being strongly attractive to being strongly repulsive very quickly. In the introduction to this chapter, we mentioned that a secondary region of attraction often occurs in DLVO systems. We found the appearance of this secondary minimum to be dependent on the chosen parameter values. Especially when using a small membrane thicknes, the secondary minimum would not occur, as is the case in Figure 4.4.

The main objective of this report however, was to find out more about the interaction between platelets of graphene, immersed in chlorosulfonic acid. In particular, our aim was to validate the claim that separate layers of graphene,



Figure 4.4: The total disjoining pressure as a function of plate separation distance $d = D/\lambda_D$ under charge regulation conditions, for the best known values of the graphene/CSA system as presented in Table 4.1. The upper dotted curve represents the repulsive double layer interactions, the lower dotted curve represents the attractive Van der Waals interactions, while the total disjoining pressure is represented by the full blue curve. Finally, the dashed vertical line represents the so-called critical distance: The separation distance of graphene layers in solid graphite.

as they reside in graphite are exfoliated by Coulombic repulsion. That is, the repulsive forces due to the electric double layer interactions need to overcome the attractive forces due to Van der Waals interactions. The critical question therefore is, what is the separation distance between layers of grapene, as it resides inside graphite on the scale of our plot. We have denoted the distance of 0.37 nm, which we identify as the critical distance, by a vertical dashed line in Figure 4.4. It is immediately apparent that this critical separation distance lies far beyond the range of repulsive interactions. The only possible conclusion we can draw from this, is that our model does not correctly explain the spontaneous exfoliation, seen in experiment [8]. Certainly, once the graphene layers are separated, we observe strong repulsive behaviour. This does explain why, once exfoliated and dissolved in chlorosulfonic acid, the separate graphene platelets remain in solution. In order to condense together, a substantial repulsive barrier needs to be overcome. In the next section, we look in depth at this result and what it means for the main question, posed at the beginning of this report.

At this point however, we want to go back to the parameter values of Table 4.1. In some instances, as for example in the case of the Hamaker constant, no specific value was available in the literature and we were forced to proceed under the assumption that the value for the graphene/CSA system does not deviate too much from the value for the graphene/water system. To the best of our knowledge, this assumption is justified, however, it remains a factor of uncertainty.

Apart from these considerations, it is at all times prudent to study how the predictions of our theory respond to varying parameter values. To this end we have, in Figure 4.5 plotted the total disjoining pressure for the graphene/CSA system once more, but this time we have varied the parameters in order to inspect their influence on the final outcome and to gauge their effect on the location of the threshold for attractive vs repulsive interactions. In the top three



Figure 4.5: The total disjoining pressure for the graphene/CSA system, as a function of plate separation distance $d = D/\lambda_D$. In the top row, the Hamaker constant \tilde{A}_H was varied, in the middle row the bulk ion density ν was varied and finally, in the bottom row, the solvent dielectric constant ϵ_r was varied. In all cases, the middle plot corresponds to the best known value of Table 4.1.

plots, we varied the Hamaker constant. In the middle plots the bulk ion density was varied and finally, in the bottom row, we varied the dielectric constant of the solvent. In all cases the middle graph corresponds to the best known value of Table 4.1. We observe that, for example by lowering the Hamaker constant, or the dielectric constant, the threshold does indeed shift closer towards the critical separation distance, denoted by the vertical dashed line. However, although we have significantly varied the parameters, in all cases the transistion still occurs quite far from the critical distance, having at least a factor of 7 for the separation distance between them. We should also point out that varying the dielectric constant ϵ_r , as well as the bulk ion density n_b changes the value of the Debye length, as $\lambda_D \propto n_b^{-1/2} \times \epsilon_r^{1/2}$. Since the critical distance, represented by the vertical dashed line corresponds to an actual fixed physical separation distance of 0.37 nm, and the separation distance on the horizontal axis is measured in units of Debye lengths, this means that the vertical dashed line moves position when either ϵ_r or ν are varied, as can be seen in the plots.

We can of course investigate how far we need to "push" our parameters, in order to actually find repulsive interaction at the critical distance. This is done in Figure 4.6, where we see that the interaction threshold lies very close to the critical distance indeed. For this plot, the values of Table 4.2 were used. From



Figure 4.6: In an attempt to find repulsive interactions at the critical distance, the values of the parameters were pushed far beyond their best known values. The repulsive behaviour at the critical distance, demonstrated in this plot was obtained using the parameter values of Table 4.2.

Table 4.2: Pushing the dimensionless parameters to find repulsion at the critical distance

Physical property	Used in Figure 4.6	Best known values
dielectric constant CSA	$\epsilon_r = 20$	$\epsilon_r = 60 \pm 10$
bulk ion density CSA	$\nu = 492.3$	$\nu = 492.3$
layer thickness graphene	h = 0.0035	h = 0.0186
maximum surface charge	$\zeta = 12.4 \times 10^4$	$\zeta = 12.4 \times 10^4$
surface reaction constant	r = 0.02	r = 0.02
Hamaker constant	$\tilde{A}_H = 0.1$	$\tilde{A}_H = 2.5$

the values in the table we see that, especially the graphene layer thickness and the Hamaker constant were pushed far beyond the best known values for our system. It is therefore questionable whether these values still correspond to a physically realistic scenario. This question, and others, are considered in depth in the next section.

4.4 Considerations and outlook

In the previous section we finally presented the main result of this report: the total disjoining pressure for the graphene/CSA system. We found, by inserting the best known values for all parameters of our system, the interaction due to the double layer and Van der Waals forces to be attractive at the critical distance. In other words, the repulsive double layer interactions are not able to overcome the attractive Van der Waals interactions and the spontaneous exfoliation of graphite in chlorosulfonic acid cannot be correctly described by our model. Even if we shift the values of our parameters somewhat, the threshold for which we find repulsion lies far beyond the critical separation distance. At first sight, this might seem like an unsatisfying result. However, this determination forces us to take a critical look at our model and think about its limitations and assumptions.

We can consider two possible explanations for not finding the repulsive interactions at the critical distance we were looking for. First, in constructing our model, several assumptions were made. Also, because of the nature of our model as a mean field theory, it inherently has its limitations. As a second explanation, one should also consider the possibility that the spontaneous exfoliation cannot be explained by electrostatics in principle. Even if our model were more refined, the combination of repulsive double layer and attractive Van der Waals interactions would lead to repulsive behaviour at the critical distance. If this were the case, additional processes and considerations need to be taken into account. Both possibilities are discussed next, starting with the limitations of our model.

First of all, our model being of mean field nature, we consider our ions to be point particles. This means we have ignored the excluded volume effect. In general, this approximation is justifiable up to a packing fraction of $\eta \approx 10\%$, which corresponds to an ion concentration of $\sim 1M$. Now, by using this value for the ion concentration, along with the bulk ion concentration of chlorosulfonic acid in the expression for the ion densities

$$n_{\pm}(x) = n_b \exp[\mp \phi(x)],$$
 (4.4.1)

we can find the maximum value of the electrostatic potential for which we can safely use the point particle assumption. We find a value of $\phi \sim \log[1/(1.735 \times 10^4)] \approx 9$. Next we can compare this to the potential at the midplane ϕ_m , for the graphene/CSA system. Note that it is safe to assume the potential between the plates to have a flat profile, such that the potential at the surfaces of the plates does not deviate too much from the midplane potential, as was shown in Section 3.3, when considering the zero field solution. In Figure 4.7, we have plotted the midplane potential for the graphene/CSA system as a function of plate separation distance. We see that, at the critical distance, the dimensionless



Figure 4.7: The dimensionless electrostatic potential at the midplane ϕ_m , as a function of plate separation distance $d = D/\lambda_D$ for the graphene/CSA system. The dotted vertical line denotes the critical separation distance.

potential is of the order of ≈ 9 . This means we are right on the threshold for the point particle assumption.

Next, we want to take a critical look at our assumption that the image charge effect is not of great importance for the graphene/CSA system. We came to this conclusion after studying the image charge effect in Chapter 3. We found that, especially for systems with a large solvent dielectric constant, the image charge effect has a limited impact on the ion distributions and disjoining pressure. However, in our model the surface charges are considered to be smooth, they are evenly distributed across the surface. In reality of course, the surface charges are located at fixed sites. According to [32], the influence of image charges on the potential is minor. However, it is also claimed [32] that considering discrete surface charges has a significant impact on the potential, due to image charge effects. This means that quantities, such as the ion densities and disjoining pressure would be affected as well. We cannot say with certainty how taking the discreteness of the surface charges into account would affect our system, but it is something that we have to remember when considering our result. Also, when considering the method by [19] in Chapter 3, we chose not to consider the electrostatic correlations between the ions. Since our system is right on the threshold for the point particle assumption, taking ion correlations into account could prove to be a valuable extension to the model.

Another simplifying assumption we made is that of mirror symmetry: In constructing our theory for two interacting membranes of finite thickness, we assumed mirror symmetry with respect to the central plane at x = 0. In reality, this mirror symmetry can be broken in several ways. One could consider the surface charges of all four surfaces to be independent, such that for example one inner surface could be more strongly charged than the other. Or, one could go one step further and consider the surface charge not to be smoothly distributed

across the surface at all. One could for example imagine patches of higher and lower surface charge forming on opposite surfaces. The first complication could easily be described by our model and would not need any new concepts, but simply requires a few more equations to be solved. The second complication on the other hand would not be very easy to implement, and would require some new ideas to be inserted into the model.

Another extension of the model that could easily be achieved is to consider multiple interacting membranes. In our model we only considered two membranes, but in reality we want to describe a system of many layers. One then obtains the setup where membranes that reside on the outside have a special status, with respect to layers that sit in the bulk of the multilayered system. This extension could prove to be very interesting and would not require any new concepts to be introduced, but would be possible by an extension of the existing model. We expect computations to become exceedingly difficult however, possibly this extension could best be studied using dedicated simulations.

Furthermore, we have assumed a basic model for the adsorption of hydrogen ions to the surface, where a single Hydrogen ion correlates with a single Carbon atom. Due to [29], we are aware that more sophisticated models are available where one hydrogen ion correlates with multiple carbon atoms. The effect of this complication on the results of our model is at this point not easily estimated.

Certainly, we need to take a critical look at the Van der Waals forces, also being of mean field nature. The expression we used for the Van der Waals free energy of interaction was taken from [20], which is a general expression for the Van der Waals interactions between two membranes of finite thickness. The value for the Hamaker constant we used was taken from [30] and is valid for a system of two graphene layers, acting across a region filled with water. As already mentioned in the main text, we were unable to find a specific value for the graphene-CSA-graphene system and therefore assumed the quoted value to be applicable to our system. This assumption seems justified, considering water and chlorosulfonic acid have similar values for their dielectric constant. However, from the plots in Section 4.3, we see that the value of the Hamaker constant is of great significance for the final results of our model. Also, as mentioned before, Van der Waals theory is a mean field theory as well. Taking into account the extremely small separation distance and membrane thickness of our system, the validity of our description of the Van der Waals forces can be questioned. A closer look at Van der Waals forces for a system with our specific characteristics seems to be a prudent step to take in a future research project.

We have not performed an extensive study into the concept of interaction energy in this report. Instead, we focussed on the disjoining pressure. For completeness, in Appendix C.1, we consider the free energy of interaction between semi-infinite parallel plates, for the surface conditions of fixed charge, fixed potential and charge regulation. We derive the free energy of interaction in three different ways: By thermodynamic integration, by statistical mechanics methods, and by deriving it from the disjoining pressure. These considerations are however not very elaborate. From [33], the experimentally determined separation energy of two 1-nm squares of graphene is over 2 eV, which can be regarded as relatively large. A more thorough study into the energetic concepts of the graphene/CSA system would however be needed to be able to say more about this. This could potentially lead to more insights into the behaviour of the system. Finally, as mentioned earlier, we also have to consider the possibility that the spontaneous exfoliation of graphite in chlorosulfonic acid cannot be explained by electrostatics in principle. That is to say, the attractive Van der Waals forces cannot be overcome by the Coulombic repulsion due to the double layer interactions alone. Other processes and considerations need to be taken into account. Specifically, a closer look at the characteristic properties of chlorosulfonic acid warrants further investigation in our opinion. In the next, final chapter, we summarize our results.

Chapter 5

Summary and final conclusions

The main goal of this report was to describe a system of graphene layers and find an explanation for the spontaneous exfoliation of graphite in chlorosulfonic acid, as found by experiment. The generally accepted explanation in the literature is that the exfoliation is caused by Coulombic repulsion, due to protonation of the graphene platelets. Hydrogen ions, formed by autodissociation of the acid bind to Carbon atoms in graphene, and are hereby responsible for its protonation.

To validate this claim, in Chapter 1 we set up a mean field theory using charge regulation to describe parallel plates of infinite thickness using DLVO theory. We constructed the grand potential for our system and from it, derived the Boltzmann distribution that describes the density profile of the ions in solution. By combining it with the Poisson equation, we arrived at the Poisson-Boltzmann equation, which lies at the heart of DLVO theory. We solved the Poisson-Boltzmann equation, both the full nonlinear version and the linearised Debye-Hückel version, for a system of one and two interacting double layers. In doing so, we considered three separate surface conditions: Fixed surface charge, fixed surface potential and charge regulation. The latter being the physically most interesting case, we focussed on setting up a charge regulation theory. Since the charge regulation case involved a selfconsistent problem, numerical computations were needed to find solutions for the electrostatic potential.

After finding solutions for the electrostatic potential, in Chapter 2 we focussed on interactions by considering the disjoining pressure between the plates. We found distinct behaviour for the cases of fixed surface charge, fixed surface potential and charge regulation conditions. Besides finding a divergent disjoining pressure for the fixed charge case, which was expected, divergent behaviour was found for the charge regulation case as well. This result is not very easy to understand and seems counterintuitive at first sight. The same results were later found to appear in the literature as well and some considerations were put forward in an attempt to explain them.

Since graphene platelets are only one layer of atoms thick, their thickness is extremeley small compared to its other dimensions. To take this property of our system into account, in Chapter 2 we focussed on describing a system of membranes: The plates were now considered to have a finite thickness. As a direct result, the outer regions on either side of the system also had to be taken into account and we had to consider four double layers, instead of two. We set up a model to describe this finite thickness effect by combining the single double layer solution and the solution for two interacting double layers. We found that the disjoining pressure between the membranes depends greatly on their thickness. For decreasing thickness, the disjoining pressure is decreased as well.

Next, in Chapter 3 we considered the image charge effect. In general, objects such as colloids have a much lower dielectric constant than the solvent in which they are immersed. This is especially true for our system of graphene platelets in chlorosulfonic acid. The mismatch in dielectric constant causes polarisation charges to form, whose effect can be described by image charges. We used two separate methods to study the image charge effect. The first consisted of solving for the potential of our system of two membranes of finite thickness, but this time taking the mismatch in dielectric constants into account. We found the result of this method unsatisfying and therefore turned our attention to a second method. In the second method, a modified Poisson-Boltzmann equation is considered. An interaction potential is introduced that describes the image charge effect. In the end, we found the effect to be increasingly small for larger solvent dielectric constants. Considering the large dielectric constant of chlorosulfonic acid, we judged the image charge effect to be of minor importance to our system.

As a small detour, the so-called zero field solution was derived. This solution for the potential between two parallel plates proved, not only very straightforward in its computations, but also capable of providing a surprisingly accurate solution for the electrostatic potential, without the need for solving the Poisson-Boltzmann equation. This appeared to be true, even beyond the range expected from the assumptions made in its derivation. Though very promising as a method for solving systems with small separation distances, the zero field method was not pursued.

The repulsive disjoining pressure due to the double layer repulsions was finally complemented by the attractive Van der Waals forces. A general expression for the Van der Waals forces between two membranes of finite thickness across an intervening medium was taken from the literature. Completing our model, we were left with finding the appropriate values for the parameters of our system. This was the subject of Chapter 4. Some parameter values were easily found in the literature, others required some derivation and in a few cases no specific values were available, forcing us to make an assumption. This was particularly true for the Hamaker constant. Of specific interest is the charge regulation parameter, which describes the adsorption of Hydrogen ions on the surfaces and is related to the binding energy. The so-called surface reaction constant was treated as a fitting parameter, an approximate value being obtained by considering a single double layer in solution and 'fitting' the parameter to obtain the degree of adsorption found by experiment.

Finally, upon inserting all parameter values, we were able to find the total disjoining pressure for the graphene/CSA system. We found that the threshold, where repulsive interactions transition to attractive interactions, occurs at a separation distance far beyond the critical distance. The critical distance being defined as the separation distance between graphene layers in solid graphite. This determination lead us to the conclusion that our model cannot correctly predict the spontaneous exfoliation of graphite in chlorosulfonic acid. The statement

often found in the literature, e.g., in [8], that the acid protonates the graphene to induce repulsion between layers, according to the results of our model, deserves to be approached with a critical mindset.

The first step in analysing our result was to take a critical look at the parameters of our system, by varying their values and determining the impact on the final result. We found that the parameters had to be varied quite far beyond their best known values, in order to find repulsive behaviour at the critical distance. The Hamaker constant in particular was found to be of great impact.

Besides the validity of our parameter values, we considered two possible explanations for our inability to correctly predict exfoliation. First, the limitations of our model and the assumptions we made. Our model, being of mean field nature, inherently has its limitations. Also, in setting up our model, we made several simplifying assumptions, including mirror symmetry and the limited impact of the image charge effect. These considerations were described in detail in Section 4.4. As a second explanation, we considered the possibility that the observed exfoliation cannot be explained by electrostatics in principle. Besides double layer repulsions and Van der Waals attractions, other processes must be taken into account. This was briefly discussed in Section 4.4.

We concluded by observing that several extensions to our model can be implemented, without the need for introducing new concepts. For example, one can consider the mirror symmetry to be broken, or consider, instead of only two membranes, a system of multiple membranes. These extensions would only add to the technical complexity of solving the equations, without the need for introducing new concepts and therefore seem like a logical next step for future research projects.

Appendix A

Appendices to Chapter 1

A.1 Definitions and notation

We have, in Table A.1 summarized the parameters used, and definitions made in this report.

	SI quantity	Dimensionless quantity
Coordinate	z	$x \equiv z/\lambda_D$
Electrostatic potential	ψ	$\phi \equiv \beta e \psi$
Bulk ion density	n_b	$\nu \equiv (\beta^3 e^6 / 8\pi^2 \epsilon_0^3) n_b$
Surface charge density	σ	$\tilde{\sigma} \equiv \lambda_B^2 \sigma$
Max. surf. charge density	σ_m	$\tilde{\sigma}_m \equiv \lambda_B^2 \sigma_m$
		$\Sigma \equiv 4\pi\bar{\lambda}\tilde{\sigma}$
		$\Sigma_m \equiv 4\pi\lambda\tilde{\sigma}_m$
		$\lambda \equiv \lambda_D / \lambda_B$
Fraction charged sites		$\alpha \equiv \sigma / \sigma_m$
Surface reaction constant		$r \equiv K/n_b$
Plate separation distance	D	$d \equiv D/\lambda_D$
Membrane thickness	H	$h \equiv H/\lambda_D$
Charge inner region	Σ^{tot}	$\Lambda \equiv \lambda_B^2 \Sigma^{tot} / e$
Disjoining pressure	П	$\tilde{\Pi} \equiv \beta \Pi / n_b$
Free energy of interaction	U	$\tilde{U} \equiv (\lambda_D^2/k_B T)U$
Prefactor image charge		$\Delta \equiv (\epsilon_{sol} - \epsilon_{obj}) / (\epsilon_{sol} + \epsilon_{obj})$
		$\gamma \equiv \epsilon_{object} / \epsilon_{solvent}$
Hamaker constant	A_H	$\left \begin{array}{c} \tilde{A}_H \equiv A_H / k_B T \right. \\ \end{array} $

Table A.1: Parameters used in this report

A.2 Deriving the terms in the Helmholtz free energy functional

In Section 1.2 we wrote down an expression for the Helmholtz free energy functional

$$\beta \mathcal{F}[n_{\pm},\sigma] = \sum_{\alpha=\pm} \int_{-\infty}^{\infty} dz \{ n_{\alpha}(z) (\log[n_{\alpha}(z)\Lambda_{\alpha}^{3}] - 1) \} + \frac{1}{2} \int_{-\infty}^{\infty} dz Q(z) \phi(z) + \sigma \{ \log[\frac{\sigma}{\sigma_{m}}] + \beta F_{b} \} + (\sigma_{m} - \sigma) \log[1 - \frac{\sigma}{\sigma_{m}}].$$
(A.2.1)

Note, that we are considering a free energy density per surface area. This is convenient since we imagine that our plates extend to infinity in both directions perpendicular to the line that connects the two plates. Here, we elaborate on how the different terms in the expression come about.

The first term represents the entropy of the ions and can be derived from Gibbs entropy equation $S = -k_B \sum_{\nu} p_{\nu} \log p_{\nu}$. Imagine that we have a total volume V filled with N ions per species. Their density is then defined as $n \equiv N/V$. Further, imagine that the volume is divided into little cubes of volume Λ^3 . The total number of cubes is then V/Λ^3 . We can now write down the probability that a cube is occupied by an ion and the probability that it is empty. They are $nV/(V/\Lambda^3)$ and $(V/\Lambda^3 - nV)/(V/\Lambda^3) = 1 - n\Lambda^3$ respectively. If we insert these expressions into Gibbs entropy equation we can obtain the entropy for a single site

$$s = -k_B \sum_{\nu} p_{\nu} \log p_{\nu} = -k_B \left\{ n\Lambda^3 \log[n\Lambda^3] + (1 - n\Lambda^3) \log[1 - n\Lambda^3] \right\}.$$
 (A.2.2)

The total entropy for V/Λ^3 sites is then given by

$$S = -k_B V \left\{ n \log[n\Lambda^3] + (1/\Lambda^3 - n) \log[1 - n\Lambda^3] \right\}.$$
 (A.2.3)

If we now let Λ become very small and use that $\log[1-x]\approx -x$ for small x, we can write

$$S = -k_B V \left\{ n \log[n\Lambda^3] - n \right\}, \tag{A.2.4}$$

which corresponds to the first term in (A.2.1) if we consider two species of ions(positive and negative), replace the volume V by an integral and multiply by -T.

The second term represents the mean-field Coulombic energy of the charges in the electric field, in general expressed as the product of the charge and the electric potential. With our charge distribution Q defined as $Q(z) \equiv n_+(z) - n_-(z) + \sigma \delta(z + D/2) + \sigma \delta(z - D/2)$ and the electric potential given by $\psi = (k_B T/e)\phi$ this works out to the second term in (A.2.1). Note, that since the potential ϕ is generated by the charge distribution Q itself there is a factor of one-half entering the expression for the energy to compensate for double counting. Also, Q needs to be multiplied by the unit charge e, which then cancels against the e from the expression for ψ . The last two terms represent the free energy of the coupling between bulk and surface. We start out again with Gibbs entropy equation $S = -k_B \sum_{\nu} p_{\nu} \log p_{\nu}$. The probability that a site is occupied is given by σ/σ_m while the probability for an empty site is $(\sigma_m - \sigma)/\sigma_m$. This gives for the free energy of coupling

$$F = U - TS = \sigma F_b + k_B T \sigma_m \left\{ \frac{\sigma}{\sigma_m} \log \frac{\sigma}{\sigma_m} + \frac{\sigma_m - \sigma}{\sigma_m} \log[\frac{\sigma_m - \sigma}{\sigma_m}] \right\},$$
(A.2.5)

where σF_b is the binding energy for occupied sites. This works out to

$$\frac{\sigma}{\beta} \{ \log[\frac{\sigma}{\sigma_m}] + \beta F_b \} + \frac{\sigma_m - \sigma}{\beta} \log[1 - \frac{\sigma}{\sigma_m}], \tag{A.2.6}$$

which corresponds to terms three and four in (A.2.1).

A.3 Deriving the Boltzmann distribution

In Section 1.2, we derive the Boltzmann distribution by minimizing the grand potential Ω with respect to the density profiles $n_{\pm}(z)$. In this appendix all steps of this derivation can be found. Starting point is our expression for the grand potential

$$\Omega[n_{\pm},\sigma] = \frac{1}{\beta} \sum_{\alpha=\pm} \int_{-\infty}^{\infty} dz \{ n_{\alpha}(z) (\log[n_{\alpha}(z)\Lambda_{\alpha}^{3}] - 1) \} \\ + \frac{1}{2\beta} \int_{-\infty}^{\infty} dz Q(z) \phi(z) + \frac{\sigma}{\beta} \{ \log[\frac{\sigma}{\sigma_{m}}] + \beta F_{b} \} \quad (A.3.1) \\ + \frac{\sigma_{m} - \sigma}{\beta} \log[1 - \frac{\sigma}{\sigma_{m}}] - \int_{-\infty}^{\infty} dz \{ \sum_{\alpha=\pm} \mu_{\alpha}(z) n_{\alpha}(z) + \mu_{+}(z) \sigma \delta(z) \},$$

which we minimize with respect to n_{\pm} :

$$\begin{split} \frac{\delta\Omega[n_{\pm},\sigma]}{\delta n_{+}(z)} &= \\ \frac{1}{\beta} \int_{-\infty}^{\infty} dz' \frac{\delta}{\delta n_{+}(z)} \left\{ n_{+}(z') \log[n_{+}(z')\Lambda_{+}^{3}] - n_{+}(z') + n_{-}(z') \log[n_{-}(z')\Lambda_{-}^{3}] - 1 \right\} \\ &+ \frac{1}{2\beta} \frac{\delta}{\delta n_{+}(z)} \int_{-\infty}^{\infty} dz' Q(z') \phi(z') \\ &- \frac{\delta}{\delta n_{+}(z)} \int_{-\infty}^{\infty} dz' \left\{ \mu_{+}(z') n_{+}(z') + \mu_{-}(z') n_{-}(z') + \mu_{+}(z') \sigma \delta(z) \right\} \\ &= 0 \quad (A.3.2) \end{split}$$

 \rightarrow

$$\begin{split} \int_{-\infty}^{\infty} dz' \left\{ \delta(z'-z) \log[n_{+}(z')\Lambda_{+}^{3}] + n_{+}(z') \frac{1}{n_{+}(z')\Lambda_{+}^{3}} \delta(z'-z)\Lambda_{+}^{3} - \delta(z'-z) \right\} \\ &+ \frac{1}{2} \frac{\delta}{\delta n_{+}(z)} \int_{-\infty}^{\infty} dz' Q(z') \phi(z') - \beta \int_{-\infty}^{\infty} dz' \left\{ \mu_{+}(z') \delta(z'-z) \right\} = 0 \\ &\qquad (A.3.3) \end{split}$$

$$\log[n_{+}(z)\Lambda_{+}^{3}] + \int_{-\infty}^{\infty} dz \left\{ \delta(z'-z) - \delta(z'-z) \right\} + \phi(z) - \beta \mu_{+}(z) = 0 \quad (A.3.4)$$

 \rightarrow

$$\to \log[n_+(z)\Lambda_+^3] = \beta \mu_+(z) - \phi(z) = \log[n_b \Lambda_+^3] - \phi(z) \text{ for } z > 0 \quad (A.3.5)$$

$$\rightarrow \log\left[\frac{n_+(z)\Lambda_+^3}{n_b\Lambda_+^3}\right] = -\phi(z) \tag{A.3.6}$$

$$\rightarrow n_+(z) = n_b \exp[-\phi(z)]$$
 for $z > 0.$ (A.3.7)

By following the same procedure, an expression for $n_{-}(z)$ can be obtained, so we finally obtain the famous Boltzmann distributions

$$n_{\pm}(z) = n_b \exp[\mp \phi(z)], \text{ for } z > 0.$$
 (A.3.8)

A.4 Deriving the Langmuir adsorption isotherm

Starting point is again the expression for the grand potential as given in Section 1.2, which we now minimize with respect to σ :

$$\frac{\partial\Omega[n_{\pm},\sigma]}{\partial\sigma} = \frac{1}{2\beta} \frac{\partial}{\partial\sigma} \int_{-\infty}^{\infty} dz Q(z)\phi(z) + \frac{1}{\beta} \frac{\partial}{\partial\sigma} \left\{ \sigma(\log[\frac{\sigma}{\sigma_m}] + \beta F_b) \right\} \\ + \frac{1}{\beta} \frac{\partial}{\partial\sigma} \left\{ (\sigma_m - \sigma) \log[1 - \frac{\sigma}{\sigma_m}] \right\} - \frac{\partial}{\partial\sigma} \int_{-\infty}^{\infty} dz \mu_+ \sigma \delta(z) = 0. \quad (A.4.1)$$

$$\rightarrow \frac{1}{2} \frac{\partial}{\partial \sigma} \int_{-\infty}^{\infty} dz Q(z) \phi(z) + \log[\frac{\sigma}{\sigma_m}] + \beta F_b + 1 - \log[1 - \frac{\sigma}{\sigma_m}] - 1 - \beta \int_{-\infty}^{\infty} dz \mu_+ \delta(z) = 0.$$
 (A.4.2)

$$\rightarrow \phi_s + \log[\frac{\sigma}{\sigma_m}] + \beta F_b - \log[1 - \frac{\sigma}{\sigma_m}] - \beta \mu_+ = 0.$$
 (A.4.3)

$$\rightarrow \phi_s + \beta F_b - \beta \mu_+ = \log \left[\frac{\sigma_m - \sigma}{\sigma} \right].$$
 (A.4.4)

$$\rightarrow \alpha = \frac{\sigma}{\sigma_m} = \frac{1}{1 + \exp[\beta F_b - \beta \mu_+ + \phi_s]}.$$
(A.4.5)

A.5 The law of mass action

In Section 1.3, we use the law of mass action to find an expression for the charge regulation parameter α . The law of mass action states that the rate of a chemical reaction is directly proportional to the product of the concentrations of the reactants. If we consider the equilibrium $S + H^+ \implies SH^+$ with equilibrium constant K, where [S] denotes the concentration of empty sites on the surface, $[SP^+]$ the concentration of sites where a positive ion has been adsorped and $[P^+]_s$ represents the density of positive ions near the surface, this gives us:

$$K = \frac{[S][P^+]_s}{[SP^+]} = \frac{\sigma_m - \sigma}{\sigma} \rho_+(0^+) = \frac{\sigma_m - \sigma}{\sigma} n_b \exp[-\phi_s]. \tag{A.5.1}$$

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Rewriting this for σ gives:

$$\sigma = \sigma_m \left\{ 1 + \frac{K}{n_b} \exp[\phi_s] \right\}^{-1}, \tag{A.5.2}$$

which finally leads to an expression for α

$$\alpha = \frac{\sigma}{\sigma_m} = \frac{1}{1 + K \exp[\phi_s]/n_b}.$$
(A.5.3)

A.6 The solution of the nonlinear Poisson-Boltzmann equation for two plates

In Section 1.5, we presented the solution to the nonlinear Poissoin-Boltzmann equation for the setup with two parallel plates. Here, we will give the full derivation of this solution, both for fixed potential and charge regulation conditions.

A.6.1 Fixed surface potential

Here, we have the additional boundary condition

$$\phi(x = \pm d/2) \equiv \phi_s, \tag{A.6.1}$$

with ϕ_s the potential at the surfaces. By inserting this boundary condition in (1.5.10) we can obtain a relation between ϕ_m , d and ϕ_s

$$\phi_s = 2 \operatorname{arcsinh}\left[\frac{\sinh[\phi_m/2]}{\operatorname{cn}[(d/2)\cosh[\phi_m/2], \frac{1}{\cosh[\phi_m/2]}]}\right],\tag{A.6.2}$$

where cn is one of the Jacobi elliptic functions known as the Jacobian cosine amplitude [34]. By inserting the obtained ϕ_m back into (1.5.10) we then have ϕ as a function of x with parameters d and ϕ_s .

A.6.2 Charge regulation

We start with the following set of equations

$$\phi''(x) = \sinh[\phi(x)]; \tag{A.6.3a}$$

$$\phi'(x=0) = 0;$$
 (A.6.3b)

$$\phi(x=0) = \phi_m. \tag{A.6.3c}$$

From the Poisson-Boltzmann equation we find

$$\frac{d}{dx}\left(\frac{d\phi}{dx}\right)^2 = 2\sinh[\phi(x)]\frac{d\phi}{dx}.$$
(A.6.4)

This can be integrated to give

$$\left(\frac{d\phi}{dx}\right)^2 = 2\cosh[\phi(x)] + C. \tag{A.6.5}$$

Using both boundary conditions we obtain

$$\left(\frac{d\phi}{dx}\right)^2 = 2(\cosh[\phi(x)] - \cosh[\phi_m]). \tag{A.6.6}$$

This can be rewritten to

$$\left(\frac{d\phi}{dx}\right)^2 = 4(\sinh^2[\frac{\phi(x)}{2}] - \sinh^2[\frac{\phi_m}{2}]).$$
(A.6.7)

Then define $t \equiv \sinh[\frac{\phi(x)}{2}]$ and $t_0 \equiv \sinh[\frac{\phi_m}{2}]$ so that we get

$$\frac{d\phi}{dx} = 2\sqrt{t^2 - t_0^2},\tag{A.6.8}$$

from which we can write

$$\frac{dt}{dx} = \frac{dt}{d\phi}\frac{d\phi}{dx} = \cosh[\frac{\phi(x)}{2}]\sqrt{t^2 - t_0^2} = \sqrt{\cosh^2[\frac{\phi(x)}{2}]}\sqrt{t^2 - t_0^2}, \quad (A.6.9)$$

which leads to

$$dx = \frac{dt}{\sqrt{(t^2 + 1)(t^2 - t_0^2)}},\tag{A.6.10}$$

by using the fact that $\cosh^2 x = \sinh^2 x + 1$. Then we integrate from x = 0 to x = x:

$$\int_0^x dx' = \int_{t_0}^t \frac{dt'}{\sqrt{(t'^2 + 1)(t'^2 - t_0^2)}}.$$
(A.6.11)

This can be rewritten to an elliptic integral of the first kind by defining $k \equiv \frac{1}{\cosh[\phi_m/2]}$ and $\alpha \equiv \arccos \frac{t_0}{t} \rightarrow dt = \frac{t_0}{\cos^2 \alpha} \sin \alpha d\alpha$ so that we get

$$x = k \int_0^{\arccos \frac{t_0}{t}} \frac{t_0 \sin \alpha d\alpha}{\cos^2 \alpha \sqrt{(t^2 + 1)k^2(t^2 - t_0^2)}},$$
 (A.6.12)

which after some manipulation works out to

$$x = k \int_0^{\arccos \frac{t_0}{t}} \frac{d\alpha}{\sqrt{1 - k^2 \sin^2 \alpha}} = kF(\theta, k), \tag{A.6.13}$$

with $\theta \equiv \arccos \frac{t_0}{t}$ and k and α as defined above. $F(\theta, k)$ is en elliptic integral of the first kind, defined as

$$F(\theta,k) = \int_0^\theta \frac{d\alpha}{\sqrt{1 - k^2 \sin^2 \alpha}}.$$
 (A.6.14)

So, the expression we have then is

$$x = \frac{1}{\cosh[\phi_m/2]} F\left(\arccos\frac{\sinh[\phi_m/2]}{\sinh[\phi(x)/2]}, \frac{1}{\cosh[\phi_m/2]}\right).$$
(A.6.15)

This expression can finally be inverted to give

$$\phi(x) = 2 \operatorname{arcsinh}\left[\frac{\sinh[\phi_m/2]}{\operatorname{cn}(x \cosh[\phi_m/2], \frac{1}{\cosh[\phi_m/2]})}\right],\tag{A.6.16}$$

where arcsinh is the inverse hyperbolic sine and again, cn is one of the Jacobi elliptic functions known as the Jacobian cosine amplitude.

Appendix B

Appendices to Chapter 3

B.1 Image charge effect: A modified Poisson-Boltzmann equation

In Section 3.1.3 we consider a modified Poisson-Boltzmann equation in order to study the image charge effect. This method is due to [19]. It starts by considering a correlational and charge-image contribution W(z), which is given in SI units by

$$W(z) = \frac{k_B T \lambda_B}{4} \int_0^\infty dk k (\frac{f_1}{f_3} \exp[2pz] \times [(p+k) \exp[2r_c p - r_c k] + (p-k) \exp[2r_c p + r_c k]] + \frac{f_2}{f_3} \exp[-2pz + 2r_c p] \times [(p+k) \exp[2Dp + r_c k] + (p-k) \exp[2Dp - r_c k]]),$$
(B.1.1)

where k is a wavevector, $p = \sqrt{1/\lambda_D^2 + k^2}$, r_c is the ion radius, D is the plate separation distance and the f_i are given by

$$f_1 = p \cosh[kr_c] + k \sinh[kr_c]; \tag{B.1.2a}$$

$$f_2 = p \cosh[kr_c] - k \sinh[kr_c]; \tag{B.1.2b}$$

$$f_3 = p(\exp[2Dp]f_1^2 - \exp[4r_c p]f_2^2).$$
(B.1.2c)

W(z) corresponds to the work necessary to insert an ion at position z and is calculated using the Güntelberg charging process. As mentioned in Section 3.1.3, we only consider the image charge effect and ignore the charge-charge correlation effect, by setting $r_c = 0$, which gives us

$$W(z) = \frac{k_B T \lambda_B}{2} \int_0^\infty dk \frac{k}{p(\exp[2Dp] - 1)} \left\{ \exp[2pz] + \exp[2p(D - z)] \right\},$$
(B.1.3)

which is the expression used in Section 3.1.3.

Appendix C

Appendices to Chapter 4

C.1 Free energy of interaction

In the main text of this report we looked at the interaction between double layers in a flat plane geometry, by considering the disjoining pressure. One can also look at the interaction energy between the plates. Here, we derive this interaction energy, which we might call the free energy of interaction, as we are also considering entropic effects. There are different ways to calculate the free energy of interaction. The first is by thermodynamic integration: We determine the free energy between two plates for a given plate distance d, and then subtract from it the free energy at infinite plate separation. This gives us the free energy of interaction due to the double layers for that particular separation distance d. Secondly, we use statistical mechanics to derive the free energy of interaction. The third method is by integrating the disjoining pressure. In this section, the equivalence of the three methods is shown. All results in this section are based on the solution of the linear Debye-Hückel equation.

C.1.1 Free energy by using thermodynamic integration

In this method, which is due to Verwey and Overbeek [12] we calculate the free energy by imagining a charging process that charges the plates from zero surface charge to the final surface charge $\tilde{\sigma}$. In our case this involves the adsorption of positive ions onto the surface.

When $d\Gamma$ ions are adsorbed onto the surface(per unit area), the corresponding change in free energy is given by

$$df = (\mu^s - \mu^b)d\Gamma, \tag{C.1.1}$$

where μ^s and μ^b are the surface and solvent bulk electrochemical potential respectively and we have introduced the free energy density f, which is a free energy per surface area. For the surface electrochemical potential we can make the definition

$$\mu^s = \bar{\mu}^s + q\psi_s, \tag{C.1.2}$$

where q is the charge of the ions and ψ_s is the surface potential. Here $\bar{\mu}^s$ is the chemical part of the surface electrochemical potential and we assume that it

does not explicitly depend on the surface potential ψ_s , but only on the amount of ions adsorbed: $\bar{\mu}^s = \bar{\mu}^s(\Gamma)$. Putting this in and integrating gives the following expression for the free energy density

$$f = \int_0^\Gamma (\bar{\mu}^s - \mu^b) d\Gamma' + q \int_0^\Gamma \psi_s d\Gamma', \qquad (C.1.3)$$

which can be written as

$$f = \underbrace{\int_{0}^{\Gamma} (\bar{\mu}^{s} - \mu^{b}) d\Gamma'}_{\text{chemical term}} + \underbrace{\int_{0}^{\sigma_{e}} \psi_{s}(\sigma'_{e}) d\sigma'_{e}}_{\text{electrical term}}, \tag{C.1.4}$$

where Γ is the surface density of the ions and $qd\Gamma = d\sigma_e$. Notice that there are two terms in (C.1.4); the first is called the chemical contribution to the free energy and the second term corresponds to the electrical work that is done in creating the double layer. It is dubbed the electrical term.

The explicit form of the free energy density in (C.1.4) depends on the specific case we are considering. For the case of charge regulation we do not have an explicit expression for ψ_s as a function of σ_m and r available. Therefore, we cannot readily determine the free energy by means of thermodynamic integration in this case. However, both for the cases of fixed surface charge and fixed surface potential, the integration can be performed as we now demonstrate.

The explicit form of the chemical term depends on the specific case and on the way in which the surfaces acquire their charge. In case of constant surface charge the density of adsorbed ions on the surface(Γ) does not change and is thus independent of the separation distance. This means that $\bar{\mu}^s(\Gamma)$ does not change and, by definition, μ^b is constant as well, meaning that in calculating the free energy of interaction the chemical term can be ignored in the case of constant σ .

For a constant surface potential we have that $\mu^s = \mu^b$ at equilibrium and so $\mu^b = \bar{\mu}^s + q\psi_s$ and from there $\bar{\mu}^s - \mu^b = -q\psi_s$ and since ψ_s is constant, the chemical term becomes

$$\int_0^{\Gamma} (\bar{\mu}^s - \mu^b) d\Gamma' = -q\psi_s \int_0^{\Gamma} d\Gamma' = -q\psi_s \Gamma = -\psi_s \sigma_e.$$
(C.1.5)

So, finally we have that

$$f^{FC} = \int_0^{\sigma_e} \psi_s(\sigma'_e) d\sigma'_e, \tag{C.1.6}$$

is the free energy density for fixed surface charge and

$$f^{FP} = \int_0^{\sigma_e} \psi_s(\sigma'_e) d\sigma'_e - \sigma_e \psi_s = f^{FC} - \sigma_e \psi_s, \qquad (C.1.7)$$

is the free energy density for fixed surface potential. So, to be able to calculate the free energy we need an expression for the surface potential ψ_s as a function of the surface charge density σ .

Fixed surface charge

For fixed surface charge σ_e the expression for the free energy per surface area is given by (C.1.6) where $\psi_s(\sigma_e)$ is the electric potential at the surfaces, given by:

$$\psi_s(\sigma_e) = \frac{k_B T}{e} 4\pi \lambda \tilde{\sigma} \coth[\frac{d}{2}] = \frac{k_B T}{e^2} 4\pi \lambda_B \lambda_D \sigma_e \coth[\frac{d}{2}].$$
(C.1.8)

To find the interaction potential between the plates, we calculate the free energy density as a function of plate separation d, and subtract from it the free energy density at infinite plate separation $d \to \infty$. After integrating we get for the free energy per surface area:

$$f^{FC}(d) = \frac{2\pi k_B T \lambda_B \lambda_D}{e^2} \operatorname{coth}[\frac{d}{2}] \sigma_e^2 = 2\pi k_B T \lambda \operatorname{coth}[\frac{d}{2}] \tilde{\sigma}^2 / \lambda_B^2, \qquad (C.1.9)$$

while for $d \to \infty$ we have:

$$f^{FC}(d \to \infty) = 2\pi k_B T \lambda \tilde{\sigma}^2 / \lambda_B^2.$$
(C.1.10)

So, the interaction potential for two parallel plates per unit surface area for fixed $\tilde{\sigma}$ is given by:

$$U^{FC}(d) = 4\pi k_B T \lambda (\coth[\frac{d}{2}] - 1)\tilde{\sigma}^2 / \lambda_B^2, \qquad (C.1.11)$$

where we have multiplied the entire expression by a factor 2 since we are considering two plates. If we define a dimensionless interaction energy for two plates in units of $k_B T$ per surface area of the Bjerrum length squared, we find:

$$\tilde{U}^{FC}(d) \equiv \frac{\lambda_B^2}{k_B T} U^{FC}(d) = 4\pi\lambda (\coth[\frac{d}{2}] - 1)\tilde{\sigma}^2.$$
(C.1.12)

Fixed surface potential

For fixed surface potential the expression for the free energy density is given by (C.1.7) which works out to

$$f^{FP}(d) = \frac{2\pi k_B T\lambda}{\lambda_B^2} \coth[\frac{d}{2}]\tilde{\sigma}^2 - \frac{e\tilde{\sigma}\psi_s}{\lambda_B^2} = -\frac{2\pi k_B T\lambda}{\lambda_B^2} \coth[\frac{d}{2}]\tilde{\sigma}^2. \quad (C.1.13)$$

Next, insert the expression for $\tilde{\sigma}(\psi_s)$

$$\tilde{\sigma}(\psi_s) = \frac{e\psi_s}{4\pi k_B T \lambda} \tanh[\frac{d}{2}], \qquad (C.1.14)$$

to obtain

$$f^{FP}(d) = \frac{-e^2 \psi_s^2}{8\pi k_B T \lambda \lambda_D^2} \tanh[\frac{d}{2}], \qquad (C.1.15)$$

as the surface free energy density for fixed surface potential. The interaction potential is obtained by subtracting the free energy for infinite seperation distance. For $x \to \infty$: $tanh[x] \to 1$ so the interaction potential per unit surface area for two plates and fixed surface potential is given by:

$$U^{FP}(d) = \frac{-e^2}{4\pi k_B T \lambda \lambda_B^2} (\tanh[\frac{d}{2}] - 1) \psi_s^2, \qquad (C.1.16)$$

where we have multiplied by an overall factor of 2 since we are considering the interaction between two plates. Rewriting to a dimensionless expression for the interaction energy gives:

$$\tilde{U}^{FP}(d) \equiv \frac{\lambda_B^2}{k_B T} U^{FP}(d) = \frac{1}{4\pi\lambda} (1 - \tanh[\frac{d}{2}]) \phi_s^2.$$
(C.1.17)

C.1.2 Free energy by means of statistical mechanics

Here, we derive the free energy of interaction by means of a different method. We determine the free energy by inserting the expressions for $n_{\pm}(z)$ and $\phi(z)$ back into the expression for the grand potential Ω . In this instance, we shall calculate the energy for the case of fixed surface charge.

Starting point of our derivation will therefore be our expression for the grand potential Ω

$$\Omega[n_{\pm},\sigma] = \mathcal{F}[n_{\pm},\sigma] - \int_{-\infty}^{\infty} dz \{ \sum_{\alpha=\pm} \mu_{\alpha}(z) n_{\alpha}(z) + \mu_{+}(z) \sigma \delta(z+D/2) + \mu_{+}(z) \sigma \delta(z-D/2) \},$$
(C.1.18)

where the Helmholtz free energy functional \mathcal{F} is given by

$$\mathcal{F}[n_{\pm},\sigma] = \frac{1}{\beta} \sum_{\alpha=\pm} \int_{-\infty}^{\infty} dz \{ n_{\alpha}(z) (\log[n_{\alpha}(z)\Lambda_{\alpha}^{3}] - 1) \} + \frac{1}{2\beta} \int_{-\infty}^{\infty} dz Q(z) \phi(z) + \frac{\sigma}{\beta} \{ \log[\frac{\sigma}{\sigma_{m}}] + \beta F_{b} \} + \frac{\sigma_{m} - \sigma}{\beta} \log[1 - \frac{\sigma}{\sigma_{m}}].$$
(C.1.19)

If we now insert the thermal de Broglie wavelength Λ_{α} , given by the following expression $\Lambda_{\alpha}^{3} = (1/n_{b}) \exp[\mu_{\alpha}/k_{B}T]$, the first term in the expression for \mathcal{F} becomes

$$\frac{1}{\beta} \sum_{\alpha=\pm} \int_{-\infty}^{\infty} dz \{ n_{\alpha}(z) (\log[\frac{n_{\alpha}(z)}{n_b}] - 1) \} + \sum_{\alpha=\pm} \int_{-\infty}^{\infty} dz n_{\alpha}(z) \mu_{\alpha}. \quad (C.1.20)$$

The second term now cancels against the second term in (C.1.18) and the full expression for Ω becomes

$$\Omega[n_{\pm},\sigma] = \frac{1}{\beta} \sum_{\alpha=\pm} \int_{-\infty}^{\infty} dz \{n_{\alpha}(z)(\log[\frac{n_{\alpha}(z)}{n_{b}}] - 1)\}$$

+ $\frac{1}{2\beta} \int_{-\infty}^{\infty} dz Q(z)\phi(z) + \frac{1\sigma}{\beta} \{\log[\frac{\sigma}{\sigma_{m}}] + \beta F_{b}\} + \frac{1\sigma_{m} - \sigma}{\beta} \log[1 - \frac{\sigma}{\sigma_{m}}]$
- $\int_{-\infty}^{\infty} dz \{\mu_{+}(z)\sigma\delta(z + D/2) + \mu_{+}(z)\sigma\delta(z - D/2)\}.$ (C.1.21)

Since what we are looking for is an expression for the interaction between two plates, it is clear that only those terms that depend on the plate seperation distance D are important. In our present consideration we can therefore safely ignore all but the first two terms. Now we are ready to insert our expressions for the ion densities $n_{\pm}(z) = n_b \exp[\mp \phi(z)]$ which gives us

$$\begin{split} \Omega[n_{\pm},\sigma] &= \frac{1}{\beta} \int_{-\infty}^{\infty} dz \{ n_b \exp[-\phi(z)] (\log[\frac{n_b \exp[-\phi(z)]}{n_b}] - 1) \\ &+ n_b \exp[+\phi(z)] (\log[\frac{n_b \exp[\phi(z)]}{n_b}] - 1) \} \\ &+ \frac{1}{2\beta} \int_{-\infty}^{\infty} dz \{ n_+(z) - n_-(z) + \sigma \delta(z + D/2) + \sigma \delta(z - D/2)) \phi(z) \}. \end{split}$$
(C.1.22)

Working it out gives

$$\Omega[n_{\pm},\sigma] = \frac{An_b}{\beta} \int_{-\infty}^{\infty} dz (\phi(z) \sinh[\phi(z)] - \cosh[\phi(z)]) - \frac{n_b}{\beta} \int_{-\infty}^{\infty} dz \sinh[\phi(z)]\phi(z) + \frac{\sigma}{2\beta} \int_{-\infty}^{\infty} dz \{\delta(z+D/2)\phi(z) + \delta(z-D/2)\phi(z)\},$$
(C.1.23)

which leads to

$$\Omega[n_{\pm},\sigma] = \frac{n_b}{\beta} \int_{-\infty}^{\infty} dz (\phi(z) \sinh[\phi(z)] - 2 \cosh[\phi(z)]) + \frac{\sigma}{2\beta} \int_{-\infty}^{\infty} dz \{\delta(z+D/2)\phi(z) + \delta(z-D/2)\phi(z)\}. \quad (C.1.24)$$

For small $\phi(z)$ we can write

$$\Omega[n_{\pm},\sigma] = \frac{An_b}{\beta} \int_{-\infty}^{\infty} dz \{\phi(z)(\phi(z) + \frac{\phi(z)^3}{3!} + \dots) - 2(1 + \frac{\phi(z)^2}{2!} + \frac{\phi(z)^4}{4!} + \dots)\} + \frac{A\sigma}{2\beta} \int_{-\infty}^{\infty} dz \{\delta(z+D/2)\phi(z) + \delta(z-D/2)\phi(z)\}, \quad (C.1.25)$$

which works out to

$$\Omega[n_{\pm},\sigma] = \frac{An_b}{\beta} \int_{-\infty}^{\infty} dz \{-2\} + \frac{A\sigma}{2\beta} \int_{-\infty}^{\infty} dz \{\delta(z+D/2)\phi(z) + \delta(z-D/2)\phi(z)\}, \quad (C.1.26)$$

if we ignore ϕ^4 and higher contributions. Now, this first term is clearly a constant and can therefore be ignored when considering interactions. This finally leads to

$$\Omega[n_{\pm},\sigma] = \frac{1}{2\beta} \int_{-\infty}^{\infty} dz \{q(z)\phi(z)\}$$
(C.1.27)

where q(z) is defined by:

$$q(z) = \sigma\delta(z + D/2) + \sigma\delta(z - D/2)$$
(C.1.28)

Inserting the expressions for q(z) and $\phi(z)$ we obtain

$$\Omega = 4\pi k_B T \lambda \coth\left[\frac{d}{2}\right] \tilde{\sigma}^2 / \lambda_B^2, \qquad (C.1.29)$$

where the expression for q(z) is used from C.1.28 and for $\phi(z)$ we have used the solution for fixed surface charge given by

$$\phi^{FC}(x) = 4\pi\lambda\tilde{\sigma}\frac{\cosh[x]}{\sinh[d/2]}.$$
(C.1.30)

Again, subtract the same expression for $D \to \infty$ to obtain the free energy per surface area which, when rewritten to our dimensionless variables looks like this

$$\tilde{U}^{FC}(d) \equiv \frac{\lambda_B^2}{k_B T} U^{FC}(d) = 4\pi\lambda (\coth[\frac{d}{2}] - 1)\tilde{\sigma}^2$$
(C.1.31)

which is the same expression as obtained in C.1.12. However, we should note that in this derivation we have assumed the dimensionless electrostatic potential ϕ to be small. As seen in the main text, this is in general not the case for our graphene/CSA system.

C.1.3 Free energy from the disjoining pressure

We already showed how the free energy of interaction can be obtained by thermodynamic integration, for the cases of fixed surface charge and fixed surface potential. However, for the case of charge regulation no explicit expression for ψ_s is available, rendering this method not readily applicable. In Section 2.3, we derived an expression for Langmuir's disjoining pressure

$$\tilde{\Pi}(d) \equiv \frac{\Pi(d)}{k_B T n_b} = 2(\cosh[\phi_m] - 1). \tag{C.1.32}$$

Now, we shall demonstrate how it can be used to find the free energy of interaction, not only for the cases of fixed surface charge and potential, but for charge regulation conditions as well. We imagine the scenario of bringing two plates together from infinite separation to a separation distance of d, against the disjoining pressure that exists between the plates. The required work to do this is then the free energy of interaction between the plates. This means we have to consider the integral

$$U(d) = \int dU = -\lambda_D \int_{\infty}^{d} \Pi dy, \qquad (C.1.33)$$

where the integration runs from ∞ to d. In this expression, we have relabeled the integration parameter d to y to avoid confusing notation. This means that y is here the separation distance between the plates, in units of λ_D . We can now perform this integral and find the free energy of interaction for the three separate surface conditions, by plugging in the appropriation expression for the disjoining pressure.

Fixed surface charge

As we derived earlier, in the case of fixed surface charge, the potential between the plates is given by

$$\phi(x) = 4\pi\lambda\tilde{\sigma}\frac{\cosh[x]}{\sinh[d/2]},\tag{C.1.34}$$

such that ϕ_m is given by

$$\phi_m = \frac{4\pi\lambda\tilde{\sigma}}{\sinh[d/2]},\tag{C.1.35}$$

and we obtain the following expression for the disjoining pressure.

$$\tilde{\Pi}^{FC} = 2(\cosh[\frac{4\pi\lambda\tilde{\sigma}}{\sinh[d/2]}] - 1).$$
(C.1.36)

We can now integrate to obtain an expression for the interaction energy

$$U^{FC} = -\lambda_D n_b k_B T (4\pi\lambda\tilde{\sigma})^2 \int_{\infty}^d \left(\frac{1}{\sinh(y/2)}\right)^2 dy$$

= $2\lambda_D n_b k_B T \times 16\pi^2 \lambda^2 \tilde{\sigma}^2 \left[\coth(y/2)\right]_{\infty}^d$ (C.1.37)
= $\frac{4\pi k_B T \tilde{\sigma}^2 \lambda}{\lambda_B^2} (\coth(d/2) - 1),$

where we have used that $\frac{d}{dx} \operatorname{coth}(\frac{x}{2}) = \frac{-1}{2\sinh^2(x/2)}$ and $n_b = \frac{1}{8\pi\lambda_B\lambda_D^2}$. This can again be rewritten to a dimensionless interaction energy in units of k_BT to find the same expression as in(C.1.12).

Fixed surface potential

For the case of fixed surface potential, the electric potential between the plates is given by

$$\phi(x) = \phi_s \frac{\cosh[x]}{\cosh[d/2]},\tag{C.1.38}$$

giving for the potential at the center between the plates

$$\phi_m = \frac{\phi_s}{\cosh[d/2]}.\tag{C.1.39}$$

Again we can insert this expression into equation (2.3.3) to obtain the disjoining pressure:

$$\tilde{\Pi}^{FP} = 2(\cosh[\frac{\phi_s}{\cosh[d/2]}] - 1).$$
(C.1.40)

Again, we can integrate to obtain the interaction energy:

$$U^{FP} = -\lambda_D k_B T \rho_b \phi_s^2 \int_{\infty}^d \left(\frac{1}{\cosh(d'/2)}\right)^2 dy$$

$$= -2k_B T \lambda_D \rho_b \phi_s^2 \left[\tanh(d'/2)\right]_{\infty}^d$$

$$= \frac{-2k_B T \lambda_D \phi_s^2}{8\pi \lambda_B \lambda_D^2} \left(\tanh(\frac{d}{2}) - 1\right)$$

$$= \frac{k_B T}{4\pi \lambda_B^2 \lambda} (1 - \tanh[\frac{d}{2}]) \phi_s^2.$$
 (C.1.41)

By rewriting this expression to a dimensionless interaction energy in units of $k_B T$ per area λ_B^2 , we again find an expression similar to (C.1.17).

Charge regulation

For the case of charge regulation, the electrical potential is given by

$$\phi(x) = C \cosh[x],\tag{(??)}$$

and its value at x = 0 by

$$\phi_m = \phi(x=0) = C. \tag{C.1.42}$$

This gives for the reduced disjoining pressure

$$\hat{\Pi}^{CR} = 2(\cosh[C] - 1),$$
(C.1.43)

where C is given implicitly by

$$C = \frac{4\pi\lambda\sigma_m}{\sinh(\frac{d}{2})(1+r\exp[C\cosh(\frac{d}{2})])}.$$
(C.1.44)

Again, we can again integrate the expression for the disjoining pressure to obtain the potential energy by means of (C.1.33). For the specific case of charge regulation, the expression for the dimensionless free energy becomes

$$\tilde{U}^{CR}(d) = \frac{\lambda_B^2}{k_B T} U^{CR}(d) = \frac{1}{8\pi\lambda} \int_d^\infty C^2 dy.$$
(C.1.45)

We now have expressions for the free energy of interaction for the cases of fixed surface charge, fixed surface potential and charge regulation conditions in equations (C.1.12), (C.1.17) and (C.1.45) respectively. They are plotted in Figure C.1.

We can now compare these plots to the disjoining pressure in Figure 2.6, where we have to remember that the plots in Section 2.3.1 were obtained by solving the nonlinear Poisson-Boltzmann theory, in contrast to the results from this section, which were obtained using linear Debye-Hückel theory. However, their general behaviour should be similar.

In Figure C.1, we again observe that the CR plot lies between the FC and FP plots, as has typically been the case in all our results. From Section 2.3.1, we have that the scaling behaviour of the disjoining pressure with plate separation distance is given by $\tilde{\Pi}^{FC} \propto d^{-1}$, $\tilde{\Pi}^{FP} \propto C$ and $\tilde{\Pi}^{FC} \propto d^{-1/2}$ for fixed surface charge, fixed surface potential and charge regulation conditions respectively, and where C denotes a constant. Note that this scaling dependence only holds for small values of d. At this point, we want to make a small analysis of how these values would relate to the scaling behaviour of the free energy, and if our findings correspond to the plots in Figure C.1. This will not be a rigourous analysis.

We start by mentioning the relation between the free energy and the disjoining pressure

$$U(d) \propto \int_{d}^{Y} \Pi dy. \tag{C.1.46}$$



Figure C.1: The dimensionless free energy of interaction $\tilde{U} = \beta \lambda_B^2 U$ between two semi-infinite plates as a function of separation distance $d = D/\lambda_D$ for fixed surface charge (FC), fixed surface potential (FP) and charge regulation (CR) surface conditions. For this plot, the parameters were adjusted in such a way that the disjoining pressure approaches the same value for large d, in all three cases. This means $\Sigma = 1.0$ for the FC case, $\phi_s = 1.0$ for the FP case and $\Sigma_m = 3.72$ and r = 1.0 for the CR case.

Since we want to look at the scaling behaviour of the free energy for small separation distance only, the integral runs to a fixed value Y. By performing this integration, for example for FP conditions, we find that the scaling behaviour of the free energy obeys $U \propto (Y - d)$. This corresponds to a straight line with a negative slope, which is exactly what we see for FP conditions in Figure C.1. Looking at the CR case, we find $U \propto \sqrt{Y} - \sqrt{d}$, which agrees with the interaction energy reaching a finite value for $d \downarrow 0$. Finally, for FC conditions after integrating we find $U \propto \log[Y] - \log[d]$, which agrees with the divergent behaviour we see in Figure C.1. As already mentioned, this was not meant as a rigorous analysis of the behaviour of the free energy for small separation distance, but according to our quick analysis, we find fundamentally different asymptotic behaviour for the three surface conditions. We find them to be in agreement with their relation to the disjoining pressure.

Bibliography

- K. S. Novoselov, A. K. Geim, S. V. Morosov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, & A. A. Firsov, *Electric Field Effect in Atomi*cally Thin Carbon Films, Science 306 - 666 - (2004).
- [2] T. Mahmoudi, Y. Wang, Y-B. Hahn, Graphene and its derivatives for solar cells application, Nano Energy - 47 - 51-65 - (2018).
- [3] J. K.Wassei, R. B.Kaner, Graphene, a promising transparent conductor, Materials Today - 13 - 52-59 - (2010).
- [4] C. Yung, W.M. Wu, M.P. Pierpoint, F.V. Kusmartsev, Introduction to Graphene Electronics – A New Era of Digital Transistors and Devices, Contemporary Physics 54(5) - 233 - (2013).
- [5] M. Lotya, Y. Hernandez, P. J. King, R. J. Smith, V. Nicolosi, L. S. Karlsson, F. M. Blighe, S. De, Z. Wang, I. T. McGovern, G. S. Duesberg, and J. N. Coleman, *Liquid Phase Production of Graphene by Exfoliation of Graphite* in Surfactant/Water Solutions, Journal of the American Chemical Society - 131 - (2009).
- [6] S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen, R. S. Ruoff, *Synthesis of graphene-based* nanosheets via chemical reduction of exfoliated graphite oxide, Carbon, Volume 45 - 1558-1565 - (2007).
- [7] T. Schwamb, B. R Burg, N. C Schirmer and D. Poulikakos, An electrical method for the measurement of the thermal and electrical conductivity of reduced graphene oxide nanostructures, Nanotechnology - 20 - (2009).
- [8] N. Behabtu, J. R. Lomeda, M. J. Green, A. L. Higginbotham, A. Sinitskii, D. V. Kosynkin, D. Tsentalovich, A. Nicholas G. Parra-Vasquez, J. Schmidt, E. Kesselman, Y. Cohen, Y. Talmon, J. M. Tour & M. Pasquali, Spontaneous high-concentration dispersions and liquid crystals of graphene, Nature Nanotechnology - (2010).
- [9] A.W. Williamson, Proc. R. Soc. London 7 (1854).
- [10] E. A. Robinson AND J. A. Cirun, The chlorosulfuric acid solvent system. Part I. Electrical conductivity, transport number, and density measurements on solutions of simple bases, Canadian Journal of Chemistry -46 - (1967).

- [11] R.J. Cremlyn, *Chlorosulfonic acid*, Royal Society of Chemistry (2002).
- [12] Verwey and Overbeek, Theory of the stability of lyophobic colloids, Elsevier Publishing company inc. - (1948).
- [13] T. Markovich, D. Andelman and R. Podgornik, *Charge regulation: a generalized boundary condition?* EPL (Europhysics Letters) - 113 - (2016).
- [14] J. Everts, Colloidal dispersions of repulsive nanoparticles PhD thesis -Utrecht University - (2016).
- [15] A. T. Valderama, Statistical thermodynamics of charge-stabilized colloids -(2008).
- [16] A. P. Philipse, B. W.M. Kuipers, A. Vrij, Algebraic Repulsions between Charged Planes with Strongly Overlapping Electrical Double Layers, American Chemical Society - (2013).
- [17] A.P. Philips, R. Tuinier, B.W.M. Kuipers, A. Vrij, M. vis, On the Repulsive Interaction Between Strongly Overlapping Double Layers of Chargeregulated Surfaces, Colloid and Interface Science Communications - 21 -(2017).
- T. Sometani, Image method for a dielectric plate and a point charge, Eur. J. Phys. - 21 - (2000).
- [19] A. P. dos Santos, Yan Levin, Electrolytes between dielectric charged surfaces: Simulations and theory, The Journal of Chemical Physics 142 -(2015).
- [20] V. Adrian Parsegian, Van der Waals Forces A Handbook for biologists, chemists, engineers, and physicists, Cambridge University Press (2006).
- [21] H. Ohshima and S. Ohki, Donnan potential and surface potential of a charged membrane, Biophys J. - 47(5) - 673678 - (1985).
- [22] A.K. Geim, Graphene: Status and Prospects, Science 2009: Vol. 324 5934
 1530-1534 (2009).
- [23] J. Fuchs, M. O. Goerbig, Introduction to the Physical Properties of Graphene, Lecture Notes - (2008).
- [24] Y.K. Koh, M.-H. Bae, D.G. Cahill, E. Pop, Reliably Counting Atomic Planes of Few-Layer Graphene (n>4), ACS Nano - Vol.5 - 1 - (2011).
- [25] J. Fang, W. G. Vandenberghe, and M. V. Fischetti, *Microscopic dielectric permittivities of graphene nanoribbons and graphene*, Physical Review B 94 (2016).
- [26] G.A. Olah, G.K.S. Prakash and J. Sommer, *Superacid Chemistry*, John Wiley and Sons - second ed. - (2009).
- [27] R.C. Paul , S. K. Vas Hkt, C. Malhotra, S. S. Pahil, J. Sci. Ind. Res. India - 21B - 528 - (1962).

- [28] V.N. Solkan and Kazanskii, MP2 study of the proton-donating power of 100% fluorosulfonic and chlorosulfonic acids, V.B. Kinetics and Catalysis - 54.3 - (2013).
- [29] Robert Pinnick, Unpublished work, (2018).
- [30] R.F. Rajter, R.H. French, W.Y. Ching, W.C. Carter and Y.M. Chiang, Calculating van der Waals-London dispersion spectra and Hamaker coefficients of carbon nanotubes in water from ab initio optical properties, Journal of Applied Physics 101 - 054303 - (2007).
- [31] W.B. Russel. D.A. Saville and W.R. Schowalter, *Colloidal Dispersions*, Cambridge University Press - (1989).
- [32] Z. Gan, X. Xing, and Z. Xu, Effects of image charges, interfacial charge discreteness, and surface roughness on the zeta potential of spherical electric double layers, The Journal of Chemical Physics 137(3):034708 - (2012).
- [33] S. Niyogi, E. Bekyarova, M. E. Itkis, J. L. McWilliams, M. A. Hamon, and R. C. Haddon, *Solution Properties of Graphite and Graphene*, Journal of American Chemical Society - 128 - 7720-7721 - (2006).
- [34] D.F. Lawden, *Elliptic Functions and Applications*, Springer Verlag (1989).