Charged Surface Interactions in Solutions of Dielectric Macromolecules

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Abstract

The behaviour of soft matter is often determined by the forces between the surfaces of its constituents (e.g. those of colloids or surfactant assemblies). These surfaces are easily charged in aqueous solutions, which often also contain macromolecules possessing “oily” hydrocarbon groups of low permittivity. Recently, for example, charged surfactant lamellar phases have been doped with uncharged water soluble polymers, producing surprising phase behaviour.

Using a simple mean field model, we have explored how the interactions between charged surfaces are modified when they interact across an electrolytic solution of dielectric spheres, considering these must electrostatically couple to the surfaces. The coupling arises from the intra—surface electric fields, which polarise low permittivity species (oil) dissolved in a high permittivity solvent (water). The model, which already predicts a reduction of surface forces due to the spheres, was extended to describe, more realistically, “dielectric polymers” between surfaces and account for the possibility of depletion. In this case, our results indicate that an account of the coupling between charged surfaces and the polymers modifies both the polymer depletion, the electrostatics and the surface forces which result from them.

Building on these results, it was possible to adapt a description accounting for coupling to predict phase behaviour of polymer doped smectics. This was contrasted to one which ignores the coupling, as is often assumed in the literature (though some researchers have pointed out the potential effect that polymers could have on the electrostatics of lamellar phases). Our phase diagrams predict that a neglect of coupling is not always a good approximation: particular experimental conditions will lead to qualitatively different phase behaviour between coupled and uncoupled approaches.

No consistent investigation of the electrostatic effects just described has been carried out to the best of our knowledge. Since the theory we have developed applies generally to any situation where neutral polymer—like solutes are dissolved in the vicinity of charged surfaces, the relevance of our findings to other interesting experimental situations will be discussed.
Declaration

I declare that this thesis has been composed entirely by myself and has not been submitted in any previous application for a degree. I have carried out the work presented, under the supervision of Mike Cates and Stefan Egelhaaf.

Ottavio Croze
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If I enjoyed the time it’s taken me to produce this thesis and if I have learnt anything useful during the experience, I owe it to several people.

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Chapter 1

Introduction

1.1 Soft Condensed Matter

Used in a conversation with a new acquaintance in a pub, the words *soft condensed matter* do not usually mean much. A few everyday examples, however, can instantly demystify the jargon: paint, milk, toothpaste, shaving gel, LCD displays, bubble bath, cornstarch, sand, cereal, DNA, cells, drug delivery etc..

The soft condensed matter physicist having the conversation, however, remains an enigmatic figure. The kind of scientist interested in DNA, cells and drug delivery is traditionally the biologist and/or the medical scientist. Paint, milk, toothpaste, LCD displays, etc. are of such obvious practical importance, that they are mostly studied by engineers/industrial scientists. And, to the punters who remember their school chemistry, paint and milk in a scientific context might recall the words “colloidal dispersion”, so that the chemist is also a potential soft matter scientist. And where does the physicist fit in? Shouldn’t he be considering “grand questions”, such as the ultimate of fate of the universe or a theory of everything?

The confusion as to the role of the soft matter physicist is justified and meaningful. On one hand, it is a reflection of the interdisciplinary nature of soft matter
research, which is indeed at the interface between physics, chemistry, biology and engineering, each of these sciences contributing its own approach (and unfortunately jargon!) to the subject. On another, it can be traced to the relative youth of soft condensed matter as branch of physics\textsuperscript{1}.

\section*{1.2 Soft Matter Physics}

So why is soft condensed matter interesting to a physicist?

From a physicist’s point of view soft matter is interesting because of its strange macroscopic behaviour. For example, vinegar can turn milk into cheese, honey doesn’t pour like water and bath foam doesn’t last. These examples highlight some key properties and related questions: stability (what makes milk a stable phase?), flow (why does honey flow in such a strange way?) and instability (why don’t foams last “forever”?).

Through experiment, theory and computer simulation, the soft matter physicist tries to understand such strange properties in terms of the microscopic constituents of soft systems and their interactions. How big the relevant “microscopic” constituents are, depends on the system of interest. The size of the constituents of all soft systems is such that the interaction between them is “weak”, so that they can be easily upset (this is what “soft” means in this context \cite{1}). To be more precise, the interactions within soft systems are weaker (and the size of their constituents bigger) than those of the atoms and molecules which determine the behaviour of other types of condensed matter, be it ordinary (simple liquids, solids etc.) or exotic (ferromagnets, superfluids, superconductors).

In this thesis we shall concentrate on “wet” soft matter, whose constituents (colloids, polymers, surfactants etc., described in Section 2.1) reside in an ordinary liquid or in an ordinary solution, known as a solvent. Often this type of system

\textsuperscript{1}Sadly, it also speaks of the lack of public exposure to the more “unfashionable” topics of scientific research.
is known as a complex fluid. For a complex fluid, an interaction is weak in the sense that it is comparable to the energy of the thermal fluctuations in the solvent. The constituents thus need to be microscopic on "brownian" scales which extend from tens of microns down to a few nanometers (from the size of the smallest surfactant micelles which make soap slippery to the biggest colloidal particles which are used in paints or foodstuffs). Thus, in wet systems, microscopic means, quite literally, a scale which can be viewed with the aid of a microscope. This is an extremely appealing feature of soft matter: its macroscopic behaviour can be studied in the kitchen, and its constituents and mechanisms can be observed directly on a monitor in a lab (or even on a kid's toy microscope).

1.3 Electrostatics in Soft and Biological Matter

The study of what is now known as soft matter has historical ties with the development of neurophysiology, the electrochemistry of solutions and electromagnetism [2]. The experiments by Luigi Galvani on the effect of electrical currents on the motion of frog legs (Fig. 1.1A) inspired Alessandro Volta to develop "voltaic piles" (batteries) (Fig. 1.1B). This made electrical currents generally available in laboratories and provided the drive for pioneering work in the effect of electricity on chemical elements and their reactions (electrochemistry), such as that of Humphry Davy, who correctly identified chemical origin of battery operation. Davy and, his apprentice, Michael Faraday showed that some elements (notably metals and their salts) in solution respond to electrical currents, and so must be electrically charged. It's not hard to imagine, considering Faraday's talent for devising meaningful experiments as research sidelines, that Faraday's pioneering studies of charged colloidal suspensions of gold [3] should follow from his pioneering work studies of electromagnetic phenomena (Fig. 1.1C). (His discovery of colloidal gold was, in fact, part of a series of experiments to test the interaction of light with matter).
Soon after the turn of the 20th century, with the “new” physics dominating the scene, research into the charged properties of soft and living materials became mainly the domain of chemistry and biology. A few notable examples of cross-breeding, however, contributed significantly to the development of all three natural sciences. For example, quantum mechanics allowed accurate evaluation of the dispersion forces used by Hamaker, Verwey and Overbeek to explain the stability of colloidal dispersions [4]. In turn, such work inspired Casimir to look for similar effects in a vacuum [5]. A similar crossfertilisation occurred in biology, where the crystallog graphical methods of X-ray scattering were used to unravel the physicochemical structure of nucleic acids and proteins, causing a tremendous advance in biological science [6]. Thanks to this work, the key role electrostatics plays in determining the structure and functional interactions of biological molecules has been recognized by the molecular biology community for quite some time (as well captured by Max Perutz [7]; see [8] for recent developments).
Large numbers of physicists have turned to the study of charged soft matter and biological systems relatively recently. Nevertheless, thanks to the developments in other areas of science and the ensuing technological advances, these are exciting times to be a soft matter physicist interested in charged systems: the tools, both theoretical and experimental, developed in the more traditional areas of soft matter (and physics in general) can be used to answer the "physical questions" that arise in biology or biologically friendly technological applications. This thesis hopes to contribute to the understanding of this exciting area of science.

1.4 Layout and Summary of Thesis Chapters

In the following chapters we shall develop a general model for the force between charged surfaces when they are immersed in an aqueous solution of salt and uncharged "fatty" polymer–like molecules.

In Chapter 2 the background physics used in our model and the current state of the understanding of soft and, more specifically, charged systems is introduced. In Chapter 3 we review some recent experiments with polymer doped lamellar phases and other systems which seem relevant to our theoretical investigation and might be used to test its conclusions (and, consequently, its assumptions).

In chapter Chapter 4 a simple mean field model (Model I) is presented. In Model I, the molecules between the surfaces are modelled as an ideal gas of dielectric spheres. Building on this simple model, in Chapter 5 we use mean field approaches borrowed from polymer physics to model the realistic situation of a solution of uncharged polymers (Model II).

Chapter 6 shows how Model II can provide an approximation to polymer doped lamellar phases and the predictions from the resulting "mapped" model are presented and discussed in Chapter 7.

To conclude in Chapter 8, after a brief summary of the original content of the thesis we make suggestions for further investigations, both experimental and
theoretical, and discuss interesting questions and ideas inspired by the work about to be presented.
Chapter 2

Background

This chapter reviews the theoretical foundations for the models we shall develop in Chapter 4 and Chapter 5. We start with an overview of complex fluids, with particular attention to those to which our models can be applied. Next, we outline the physical theories that we have used to construct our models. Some of these are well established descriptions (e.g. the Debye–Hückel theory of electrolytes and the Flory–Huggins theory of polymer solutions), which are well documented in most standard colloid science or polymer textbooks. Schematic outlines of these theories are, however, included for the sake of completeness and to provide useful results which will be needed in other parts of the thesis. The rest of the material is more advanced, and will consequently be treated in reasonable depth. To conclude the chapter, the current issues in charged soft systems will be discussed.

2.1 Complex Fluids and Mixtures

As we saw in the introduction, soft matter physics concerns itself with systems whose macroscopic behaviour is governed by the interactions of their constituents on a “mesoscopic” scale. Such constituents are often large molecular aggregates
traditionally classed into the categories of colloids, surfactants and polymers.

2.1.1 Colloids

In so far as its specific chemical nature can be ignored, a spherical colloid is the simplest constituent of a complex fluid: a microscopic ball (with a typical radius of \( \sim 0.1 - 10 \mu m \)).

Grafting a short polymer to the surface of a colloid (so as to stabilise it against Van der Walls forces mentioned in Section 2.1.5) makes it a very good approximation to a "hard sphere", having no interactions with its neighbours except for excluded volume repulsion. Hard spheres are thus brownian particles (they diffuse around fuelled by the random thermal fluctuations of the solvent) whose phase behaviour is controlled by crowding. This is probably the best understood and extensively studied colloidal system [9].

Even so, the behaviour of colloidal dispersions, even when they are not mixed with other components, can be far from trivial and is still very alive as a subject of research, especially when it comes to considering "non equilibrium" behaviour such as glassiness, jamming, hydrodynamic interactions caused by the surrounding solvent [10] or the effects of size polydispersity [11, 12].

In addition, the behaviour of colloids can be affected if the colloids are charged [13] or mixed with polymers (Section 2.1.4) or both.

2.1.2 Polymers

Polymers are chainlike repeated arrangements of chemically identical units; they exist in a variety of shapes and forms, and can be engineered to have very different properties (see the Introduction of [14]). The radius of gyration (a measure of the

\[ ^1 \text{By this we mean our emphasis is on the behaviour determined by the general physical properties (shape, charge etc.) which are brought about by chemical processes whose details do not affect the behaviour of interest.} \]
size occupied by the polymer chain) of a synthetic polymer in solution is typically in the range 10 – 100 nm.

Major advances in understanding the general features of their mechanical and thermodynamical behaviour have been possible by considering their “physical” properties alone [15]. The equilibrium [14, 15, 16] and dynamical [14, 15, 17] properties of solutions (polymer+solvent) or blends (polymer+other polymer) of monodisperse polymers are well established. In Section 2.3 we will consider the simple mean field description behaviour of polymer solutions, with a brief mention of scaling approaches.

However, the effects of polydispersity, the surfactant–like properties of block copolymers, and the modified behaviour of strange chain geometries (stars, branches etc.) (see [14] and references therein) are just a few of the areas of polymer physics which still exhibit interesting behaviour that needs to be understood. Another important area is that of charged polymers (see Section 2.6.4).

2.1.3 Surfactants and Self Assembly

A surfactant (or amphiphile) is a molecule comprising two portions, one of which has affinity with the solvent (lyophilic) and another which doesn’t (lyophobic). The most common and useful surfactants dissolve in water: they consist of long hydrocarbon chains connected to a water–soluble group. The groups are usually asymmetric so that the long part is called a tail and the short group a head. Surfactants on their own are large molecules (a few Å in length), but not mesoscopic, as in the case of colloids and polymers.

The equilibrium description of the self–assembly of surfactants into aggregates is well established [18]. Such a description uses energetic and packing considerations to predict what aggregates are stable under certain conditions: the smallest aggregates are called *micelles* and these can grow into more complicated shapes, depending on the geometry and concentration of the surfactants. For example
spherical micelles, wormlike micelles (polymer–like assemblies resembling worms) and lamellar phases are made of surfactants which increasingly favour a flat geometry.

The present day problems in the investigation of surfactant systems include the precise mechanics of the assembly (how to surfactants aggregate and how one stable aggregate transforms the next as conditions are changed) or dissolution (how surfactant assemblies fall behave when they are contacted with water), the flow properties and flow induced phase changes and the behaviour when subjected to external fields (see the contribution by Roux to [19]).

2.1.4 Mixtures

In Nature or in applications, colloids, polymers and surfactants are often mixed together.

Such mixtures are increasingly the subject of investigation by physicists in the soft community (chemists have been at it for years!). Colloid–polymer mixtures provide a paradigmatic example: when nonadsorbing polymer is added to a colloidal suspension, it induces an attraction which dramatically modifies the phase behaviour of the suspension with respect to the hard sphere case [20]. Similarly, polymer can be added to surfactant phases and this has been shown to have a significant effect on self assembly and on the phase behaviour of aggregates [21, 22]. In Chapter 3 we will describe the effect of polymers on lamellar phases.

Recent work on mixtures has been inspired by biomedical applications. Lamellar phases, surfactant vesicles, or star–polymers are studied when mixed with polymers since they may help to transport drugs (or genetic material), which are often in a polymer state, to specific biological sites [23].
The incessant molecular motion of the solvent in which colloids, polymers and surfactants live, means that their behaviour results from the competition between thermal fluctuations and fundamental interactions.

The size of colloidal systems means the effect of gravity is often unimportant\textsuperscript{ii}. The important interactions are fundamentally electrostatic or quantumelectrodynamic (dispersion forces) in origin: charged entities interact electrostatically, and surfaces across a dielectric gap attract because of the quantum fluctuations. Even excluded volume can be thought of as having fundamentally electrostatic origin, since it is due to the short range Coulomb repulsion between molecules.

The complicated many body behaviour of a system can also be successfully described by “effective interactions”. For example, effects which have entropic origin, such as “depletion induced attraction” (Section 2.3.2), can often be approximately described in terms of two body potentials (see the contribution by Frenkel in [19]). Similarly, the interaction of charged objects across an electrolyte solution can be described in terms of screened coulomb interactions and Van der Waals forces, an approach known as DLVO theory [18, 24]\textsuperscript{iii}.

The electrostatics of complex fluids will be described in the next section, and the polymer physics at the heart of depletion interactions will be mentioned in Section 2.3.2. Other specific effects, such as hydration and Helfrich forces, will be outlined in Chapter 3, for the case of lamellar phases.

\textsuperscript{ii}This typical size must be smaller than \(\approx 1 \mu m\), as is easily found by equating the gravitational potential energy associated displacing a colloid by its radius to thermal energy.

\textsuperscript{iii}the acronym stands for the names of its independent originators: Derjaguin and Landau [25] in the ex Soviet Union; Verwey and Overbeek [26] in the Netherlands.
2.2 Charged Systems In Solution

Charging Mechanisms

A common cause for the appearance of charge in solutions is ionization, favoured by commonly employed polar solvents such as water. Molecular salts, many surfactants and macromolecular or macroscopic surfaces (e.g.: colloidal particles or the container of the solution) possess ionizable groups which dissociate when placed in polar solvents (the high dielectric constant of the solvents lowers the binding energy enough that the gain in entropy of an unbound pair is greater than the loss of binding).

Besides ionization, there exist other mechanisms for which surfaces or macromolecules can acquire charge, such as ion entrapment or ion substitution [27].

Macroion Surfaces and Electrolytes

As we have seen, systems of all sizes can acquire charge in solution. We make here the distinction between macromolecular and molecular charged systems.

Macromolecular charged systems are charged surfaces or macromolecular assemblies, often called macroions, with which we can associate a charge bearing surface, e.g. colloids, surfactant aggregates or, in some descriptions, collapsed polyelectrolytes\(^\text{iv}\). Before acquiring charge, these surfaces are neutral; the ions in the vicinity of the surface, known as counterions, will thus always bear an equal and opposite charge. Some ions are bound by electrostatic attraction to the surface within what is known as the Stern or Helmholtz layer. Others, because of thermal agitation, form a diffuse atmosphere surrounding the surface known as the Gouy or diffuse layer.

The other charged entities found in a liquid solution are ionised molecular species, or dissociated salts such as NaCl. A solution containing oppositely charged ions

\(^{\text{iv}}\)Swollen polyelectrolytes are often modelled as carrying a one dimensional "line" of charge.
formed e.g. by ionically bonded salt, is known as an electrolytic solution or electrolyte. Macroions often dwell in such solutions: polyelectrolytes, such as DNA and proteins, are usually found in a 0.2M salt solution under physiological conditions.

The combination of the Stern and diffuse layers, which will also contain electrolyte ions if salt is added, is called electrical double layer and is shown for a generic surface in Fig. 2.1. How does one go about describing the physics of double layers?

### 2.2.1 Debye–Hückel and Gouy–Chapman Theories

If one adopts a molecular viewpoint, the theoretical description of ions and macroions in a liquid seems a daunting task (the solvent alone can be horriby complicated, e.g. water). A few simplifying approximations, can, however,
lead to a tractable problem. These are at the basis of the Debye–Hückel theory [28, 29, 30, 31] of electrolytes and the Gouy–Chapman [32, 33, 24] model of the double layer. In these theories, the solvent is treated as a dielectric continuum of permittivity $\varepsilon$ and the ions as a gas of point particles. This approximation, allows for the construction of solvable models, the simplest of which make an additional mean field approximation, based on the assumption that electrostatic interactions do not dominate the thermal fluctuations of the solvent.

**Mean Field Approximation: the Poisson–Boltzmann Equation**

We are interested in calculating the thermodynamic properties of a gas of point charges, either in a bulk solution or in the proximity of a surface.

A statistical mechanical approach, starting from the partition function of the system, is easily set up. However, since the potential energy of the hamiltonian contains electrostatic terms, not much other progress can be made without further approximations. This is because of the long range nature of the Coulomb interaction couples all charges to all other charges.

As for many other similar situations in physics, one way to tackle such problems is to eliminate such couplings by assuming a mean field with which each particle interacts and which is self-consistently calculated from the average effect of all other particles.

In the case of ions, the quantity we are interested in calculating is the thermally averaged electrostatic potential $\langle V(r) \rangle$ at a position $r$. Performing such averaging on both sides of the Poisson equation of electrostatics (see Section 2.5.1), we have:

\[ \varepsilon \nabla^2 \langle V \rangle = -\langle \rho \rangle \]

(2.1)

where the relativity permittivity $\varepsilon$ (for convenience we set $\varepsilon_0 = 1$ throughout
2.2. **CHARGED SYSTEMS IN SOLUTION**

this thesis) of the solution has been assumed to be uniform \(^{v}\). The solution of Equation (2.1) provides us with the desired \(\langle V(r) \rangle\) for a given test charge at \(r\). \(\langle \rho(r) \rangle\) is the average charge density at \(r\), we can express this in terms of the positive (anion) and negative (cation) number densities \(\langle n_i \rangle\):

\[
\langle \rho(r) \rangle = \sum_{i=+,-} q_i \langle n_i(r) \rangle
\]

where \(q_i = e|z_i|\) is the charge of each ion (\(e\) is the elementary charge and \(z_i\) is its valence). For the case of the charged surface, this includes counterions and salt ions which are only distinguished by their sign and valence.

\(\langle n_i(r) \rangle\) is the average of the local number density of ion \(i\) at \(r\). This average could, in principle, be evaluated if we knew the partition function of the system, which we don’t! Applying the mean field philosophy, we replace the true effect of the ions, as expressed by \(\langle V(r) \rangle\) with a mean field potential, \(V_{MF}\). This approach amounts to ignoring all but the weakest correlations between ions \([30]\) and is only a good approximation for weak electrostatic interactions or high temperatures \([29, 31]\).

In this scenario \(\langle n_i(r) \rangle\) becomes a Boltzmann factor, setting \(k_B = 1\) for convenience (as we will do in the rest of the thesis):

\[
\langle n_i(r) \rangle = n_i^* e^{-q_i V_{MF}/T}
\]

where \(n_i^*\) is the average density of ions \(i\) far away from a central ion or a surface. Substituting this expression in Poisson’s equation we thus obtain the Poisson–Boltzmann equation for the mean field potential, which we shall indicate simply with \(V\) from now on:

\[
\epsilon \nabla^2 V = - \sum_{i=+,-} q_i n_i^* e^{-q_i V/T}
\]

\(^{v}\)The case of inhomogeneous permittivity will be treated in Chapter 4. The arguments presented here are easily extended to that situation.
Equation (2.4) can thus now be solved for $V(\mathbf{r})$.

Note that far away from an ion or a charged surface we expect the system to look electrostatically neutral on average:

$$\sum_{i=+, -} q_i n^r_i = 0 \quad (2.5)$$

It is the deviations from this neutral state in the neighborhood of an ion which are at the heart of the electrostatic contribution to the free energy of an electrolyte and of the electrostatic influence of ionised surfaces.

**Debye–Hückel Linearised Equation and Debye length**

When the electrostatic energy of an ion in the potential $V$ in units of thermal energy is small, $q_i V / T \ll 1$, the Boltzmann factor can be linearised: $e^{-q_i V / T} = 1 - q_i V / T + \mathcal{O}(q_i^2 V^2 / T^2)$. This will be the case for surfaces with small surface potentials or for very dilute electrolytes.

The linearised Equation (2.4) is then:

$$\varepsilon \nabla^2 V = -\sum_{i=+, -} q_i n^r_i + \sum_{i=+, -} n^r_i q_i^2 V / T \quad (2.6)$$

and since $\sum_{i=+,-} q_i n^r_i = 0$ by electroneutrality condition (2.5), we have

$$\nabla^2 V = \kappa^2 V \quad (2.7)$$

where

$$\kappa \equiv \sqrt{\frac{\sum_i n^r_i q_i^2}{\varepsilon T}} = \frac{1}{\lambda} \quad (2.8)$$
2.2. CHARGED SYSTEMS IN SOLUTION

is the inverse of the Debye length \( \lambda \), which is a measure of the spatial correlation between charges in solution. Equation (2.7) is known as the Debye–Hückel equation. If the reservoir ions are monovalent (2.8) becomes:

\[
\lambda = \sqrt{8\pi l_B n_i^*}
\]  

(2.9)

where \( l_B = e^2/4\pi\varepsilon_0 k T \) is the Bjerrum length (the distance at which the potential energy of a pair of ions equals the thermal energy \( T \)) and for monovalent ions, \( q_i = e \). In water at room temperature is \( l_B \approx 7 \text{ Å} \). Equation (2.9) can be usefully recast as a useful formula for evaluating \( \lambda \) in nm from the salt concentration \( n_i^* \), expressed in M (and so renamed \( c_i^* \)):

\[
\lambda (\text{nm}) = 3.04/\sqrt{c_i^*(\text{M})}
\]  

(2.10)

Similar relations can be obtained for ions of different valencies (equations 12.37 of [18]).

Boundary Conditions at a Charged Surface

To find a solution to Equations (2.4) or (2.7) we need to complement them with boundary conditions, which follow from classical electrostatics. Recall at the boundary between two dielectric media 1 and 2 [34]:

\[
(D_1 - D_2) \cdot n_2 = \sigma_f
\]  

(2.11)

\[
(E_1 - E_2) \times n_2 = 0
\]  

(2.12)

where \( n_2 \) is a unit normal outwardly directed into medium 1 from medium 2, \( \sigma_f \) is the density of free charge at the surface, and \( D \) and \( E \) indicate the electrical displacement and field respectively. Equations (2.11) and (2.12) provide a
restraint on the normal components of $\mathbf{D}$ and the tangential components of $\mathbf{E}$ at the dielectric interface between two media of permittivity $\varepsilon_1$ and $\varepsilon_2$.

To apply (2.11) and (2.12) to a double layer, let medium 1 approximate electrolyte solution and medium 2 the material possessing a charged surface (e.g., a lipid bilayer or a colloid). We assume there is no electric field within medium 2 ($\mathbf{D}_2 = 0 = \mathbf{E}_2$), so that at a charged surface we require the conditions:

$$\mathbf{D}_s \cdot \mathbf{n}_s = -(\varepsilon \nabla V)_s \cdot \mathbf{n}_s = \sigma \tag{2.13}$$

where the subscript $s$ has been used to relabel the unit normal to the surface and to denote the evaluation of the surface fields and we have used the constitutive relation for locally homogeneous dielectrics $\mathbf{D} = \varepsilon \mathbf{E}(\equiv -\varepsilon \nabla V)$. (2.13) allows the determination of the potential gradient at the surface from knowledge of the surface charge density. Note that, since it is a condition on (local) fields at a surface, Equation (2.13) will hold generally, and in particular for media of non-uniform permittivity.

Since (2.4) and (2.7) are sets of second order equations the above condition needs to be complemented by another boundary condition. In the case of an isolated surface, for example, such a condition comes from requiring a vanishing value of the field on the surface bounding the region where the electrolyte resides (excluding the surface). The latter condition is equivalent to a statement of the (average) electroneutrality of a bulk electrolyte. The case when the boundary is provided by opposing surfaces is discussed in the next section for symmetric surface geometries.

Finally, we point out that the electrostatic potential is defined up to an additive constant so that when expressing boundary conditions a choice must be made for the location of the 0 of the electrostatic potential.
2.2.2 Boundary Conditions for Two Opposing Surfaces

As we shall see in Chapters 4 and 5, the solution of (2.4) or (2.7) allows us to find the electrostatic contribution to the interaction between two opposing surfaces as a function of their separation. To find such solutions, boundary conditions are necessary to fix the electric field and/or the potential as explained above.

Symmetry Requirements

For simple, highly symmetric surface geometries one of the boundary conditions follows from a symmetry requirement. For example, symmetry requires that the electric field vanish (by cancellation) midway between equally charged flat surfaces facing one another. This furnishes a condition on the gradient of the potential at the midplane: \( \nabla V|_{\text{midplane}} = 0 \).

Fixed Surface Potential and Surface Charge

For calculational convenience, it is also often assumed that either the surface charge or the surface potential remain fixed as charged surfaces approach. That is to say, either \( V_s \) or \( -\nabla V|_s \) are known\(^{vi}\). Thus, if another boundary condition is also known elsewhere (e.g. by symmetry, as in the previous subsection), then the interaction between surfaces can be calculated from the solution of the electrostatic Equations (2.4) or (2.7).

Charge Regulation

The above assumption of fixed charge or potential is not realistic. As mentioned, real charged surfaces are made of ionizable groups in equilibrium with the neighboring solution of dissociated ions. Ionization is maintained by thermal agitation.

\(^{vi}\)Both cannot be known prior to solution of the electrostatics, since the knowledge of the other depends on the functional form of the solution, by the relation between field and potential.
against binding energy which would recombine the ions. As surfaces are brought together, the electrolyte screening the surface is expelled via the Donnan effect (see next subsection) causing an increase in the surface potential. Further, the counterions which surround the surface are increasingly confined (for osmotic and electrostatic reasons) by the surfaces. Such confinement reduces the ion entropy, causing them, for small enough separations, to recombine with the surface. We deduce that in general the electrostatic state of the system involves a "dynamical" adjustment of charge and potential, on approach. This phenomenon, known as charge regulation, is controlled by the surface energetics for which different chemical models exist (see 12.13 of Israelachvili [18], or [35], and references therein) and whose precise mechanics are related to effects beyond mean field descriptions (Section 2.6).

Thus an accurate description of electrostatics would account for charge regulation. However, we can notice the following [18, 35]: the regulation process only sets in at small surface separations (once most of the salt has been expelled); fixed charge or fixed potential boundary conditions provide an adequate approximation at large distances, and useful bounds for the force between surfaces at short distances (constant charge provides an upper limit on the force and constant potential a lower one). At very short distances a whole zoo of other effects (e.g. hydration, ion correlation forces) come into play. Some of these effects are reasonably understood, others are a matter of current debate (for a few "electrostatic" examples see Section 2.6).

2.2.3 The Donnan Effect: Salt Expulsion

Often it is convenient to imagine a solution of macroions in contact with an electrolyte (salt) reservoir via a membrane which only lets ions through, but not macroions. Let us consider, for simplicity, the case of a monovalent electrolyte whose ions are indistinguishable from the macroion's counterions (these arguments can be generalised to multivalent ions). The situation of interest is shown
in Fig. 2.2. Compartments I and II are subject to the requirement of electroneutrality. Because of this, the surface charge of each macroion, which we will assume to be positively charged, needs to be compensated by an appropriate number of negatively charged ions. In addition, for each positive ion in compartment I, by electroneutrality, there will, on average, need to be a negatively charged ion. Since the macroions cannot cross the membrane, they constrain a "neutralizing" amount of negative ions to reside, on average, in section I. Thus, the amount of "free" negative ions (not involved in compensating the macroion charge) which can reside in I will be limited. Correspondingly, the concentration of electrolyte (positive ions)\(^\text{vii}\) in compartment I will be smaller than in II, an effect known as the Donnan effect [36]. One can think of the excess of free charge in I as generating a difference in the electrostatic potential between I and II: the Donnan potential.

It should be noted that while the Donnan effect is sometimes useful for to interpret

\(^\text{vii}\) By electroneutrality the concentration of positive ions and of electrolyte is the same.
results in charged systems (such as salt exclusion from lamellar phases [37]), it
is built in any statistical thermodynamic treatment of charged systems through
the requirement of electroneutrality. Examples of such treatments are Warren’s
model for void formation in charged colloidal systems [38] or our own adaptation
of the Gouy–Chapman model, presented in Chapters 4, 5 and applied to lamellar
phases in Chapter 6. In the case of charged lamellar phases in contact with a
salt reservoir, for example, the Donnan potential is identical to the mean field
electrostatic potential at the midplane between bilayer surfaces, calculated from
the Poisson–Boltzmann Equation (2.4) and suitable boundary conditions. These
arguments can be shown to hold generally, by means of the contact value theorem
(see, e.g., the contribution by M. Deserno and C. Holm to [39]), for any situation
which can be described by a cell model [40].

**Systems with Fixed Salt Content**

Real systems are often not in contact with salt reservoirs. However, when they
phase separate, salt will partition between the phases. We will consider these
matters further when contrasting our results with the experiments on polymer
doped lamellar phases in Section 7.5.

**2.2.4 Domains of Applicability**

**Poisson–Boltzmann or Debye–Hückel?**

The Debye–Hückel linearised formalism is preferable to the Poisson–Boltzmann
treatment because of its simple, linear form. This form implies that many analyt-
ical solutions to Equation (2.7) can be obtained for a variety of idealised highly
symmetric geometries, which may sometimes be a good starting point for the
initially idealised description of a complicated system.

Even outside its domain of validity, the linearised approach makes reasonable
qualitative predictions for the electrostatics around a charged surface. The ionic
concentration profiles about a surface or between surfaces, however, are poorly described by Debye–Hückel linearised theory; e.g. the predicted electrolyte density can become negative (as shown in Figures 4.6 and 4.7 of Chapter 4). This makes the linearisation an undesirable feature if one wants to account, in the mean field, for the ion (and so salt) balance in a system, and their effect on the electrostatics. It is thus convenient to find a condition for the validity of the Debye–Hückel approximation. When this condition is violated, we can be sure that the solutions to the Debye–Hückel equation provide a poor description of the ion balance.

The linearisation inherent in the Debye–Hückel approximation is only valid when the electrostatic energy of an ion at the surface is weak: $q_i V_s / T \ll 1$ (symbols defined earlier). For monovalent ($q_i = e$, $z_i = 1$) ions at room temperature, we thus require (with $k_B = 1$, as usual):

$$ V_s \ll \frac{T}{e} \simeq 25 \text{ mV} \quad (2.14) $$

When solving a problem assuming fixed potential boundary conditions the above condition is good enough. However, when the surface charge is assumed fixed, the solution of the equation is required to evaluate the surface potential (whose value depends on far away charges such as those borne by other surfaces and/or salt ions). We can estimate the potential by assuming the Debye–Hückel linearisation holds. For an isolated surface in the Debye–Hückel limit, the surface potential is $V_s = \sigma \lambda / e \ll T / e$. So to have a small surface potential we require (once more $k_B = 1$ and $\epsilon_0 = 1$):

$$ \sigma \ll \frac{\epsilon T}{e \lambda} \quad (2.15) $$

For example, for a charged surface in a 0.01 M (\( \lambda \approx 3 \text{ nm} \)) aqueous electrolyte (of relative permittivity \( \approx 80 \)) at room temperature we require $\sigma \ll 0.006 \text{ C m}^{-2}(0.04 \text{ e nm}^{-2})$.

In reality, for surfaces approaching at fixed charge the surface potential will rise
indefinitely, so that the linearisation will inevitably break down at small separations. However, it is hard to estimate where it will break down before solving the full Poisson–Boltzmann equation for the problem.

**Success and Limitations of the Gouy–Chapman Model**

The Gouy–Chapman model has been very successfully tested by experiments to probe the interaction between charged surfaces. For example, the electrostatic interaction between charged bilayers have been measured by Cowley et al. [41] in the case of a "saltless solution" and successfully compared with the prediction of the Poisson–Boltzmann equation when a surface charge density of 1 elementary charge per 14 nm$^2$ is taken to reside on the surface. In reality, the amount of charge on the surface predicted from the bilayer composition is 1 elementary charge per 7 nm$^2$, but the fraction of this which is ionised remains unknown. When comparing the experiment to the theory, the charge is thus arbitrarily assigned as that providing the best fit. Such arbitrariness as to the degree of ionisation of a charged surface in an electrolyte is an unfortunate consequence of the lack of precise knowledge of the microscopic processes which govern the surface physics. Progress is being made on this front (see Section 2.6.2), but for the moment surface charge and potential need to be measured rather crudely by other methods (e.g. electrophoresis [24, 27]).

Many other successful tests of the Gouy–Chapman theory, justifying its widespread use in modelling charged systems, have been performed in the absence and in the presence of salt [18]. Solutions to the theory for spherical surfaces and the addition of Van der Waals interactions led to the development of DLVO theory, mentioned in Section 2.1.5, which can be used to explain the main features of electrostatically stabilised colloidal dispersions [24].

The success of the Gouy–Chapman model, when the somewhat dubious approximations on which it rests are considered, is often attributed to a happy cancellation of effects. Whatever the reasons, an increasing number of situations
exist where violations can be found. These are indeed often connected with a breakdown of the approximations, in particular the mean field and continuum approximations, at distances comparable with the molecular sizes. Some of these recent subjects of investigation will be discussed in Section 2.6.

2.3 Polymer Solutions

As mentioned previously, polymers are often added to colloidal or surfactant systems. In this section we discuss the physics of polymer solutions, with particular emphasis on mean field descriptions.

General Features of Polymer Solutions

Polymer solutions are usually classified according to the concentration of dissolved polymer. A schematic pictorial view of this classification is shown in Fig. 2.3 and explained below.

A dilute polymer solution is essentially a gas of weakly interacting chains. The interactions between polymers are driven by the contact repulsion between the monomers of each chain and are thus characterised by the chain size, which can be determined experimentally by light, X-ray or neutron scattering techniques.
or viscometric measurements. The former techniques probe the pair correlations between monomers on a chain, described by a pair correlation function from which a measure of the chain size can be obtained: the \textit{radius of gyration} $R_G$ of the polymer$^{\text{viii}}$. The latter probe the flow properties of a solution of chains and thus provide an alternative measure of the chain size: the \textit{hydrodynamic radius} $R_H$ of the polymer.

As the concentration of polymers in a dilute solution is increased, a crossover concentration will be reached for which chains start to overlap and interpenetrate: the \textit{overlap concentration}. At overlap, the chains interact strongly.

As the concentration is further increased, but the concentration of monomers is still small, the solution enters the \textit{semidilute} regime. Here the interpenetration becomes more significant and the chains form a strongly interacting mesh, whose characteristic lengthscale $\xi$ is the size of the holes in the mesh, since it is on this lengthscale that significant interactions between monomers take place (see Section 2.3.2 for a mean field picture of the same process).

The \textit{concentrated} regime is reached once the concentration of monomers is very high. This becomes a \textit{melt} if all the solvent is removed from the system. Counter-intuitively, chains in a melt are ideal because of a cancellation pair interactions between chains $^{15}$. Residual (screened) interactions are also weak in concentrated polymer solutions, which are consequently well described by a mean field approach: the Flory–Huggins theory of polymer solutions.

### 2.3.1 Flory–Huggins Theory

A simple but successful description of moderately concentrated polymer solutions is provided by the Flory–Huggins $^{42, 43, 44, 16}$ mean field theory. The theory allows an evaluation of the free energy of a polymer solution by considering the possible arrangements and interactions of polymers on a lattice. The mean field
nature of the theory arises from the fact that both the arrangements and the
interactions are evaluated using the average monomer volume fraction, $\phi$, as the
probability that a site is occupied.

The Flory–Huggins Helmoltz free energy per unit volume is:

\[ f_{FH} = \frac{T}{a^3} \left[ \frac{\phi}{N} \ln \frac{\phi}{N} + (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi) \right] \]  

(2.16)

where $a$ is the lattice spacing (on a cubic lattice), $N$ is the number of monomers
in a chain (the chain length in dimensionless units) and $\chi$ is the Flory interaction
parameter.

The first two terms are entropic: the first referring to the chain and the second
to the solution. The entropic contribution is identical to that of an ordinary
molecular mixture except that the arrangements of one of the components (the
polymer's monomers) are restricted to belonging to a chain of $N$ monomers. Just
as for ordinary mixtures, the entropic terms always favour mixing.

The third term is energetic and represents the net effect of the interactions (re-
spectively): $E_{PP}$, between the molecules; $E_{SS}$, between solvent molecules; and
$E_{SP}$ between polymer and solvent molecules. Such net effect is represented by
the Flory parameter $\chi = [E_{PS} - (E_{SS} + E_{PP})/2]/T$. Depending on the sign of $\chi$
the energetic contribution can favour ($\chi < 0$) or oppose ($\chi > 0$) mixing. $\chi$ thus
provides a good measure of the quality of the solvent. For $\chi = 1/2$, the so called
theta point, there is no net interaction. If $\chi$ is greater than 1/2 Flory–Huggins
theory predicts the possibility of phase separation, since then the free energy has
potentially antithetic entropic and energetic contributions. Because of this sign
reversal in the interaction term, a polymer in solution is said to reside in a poor
solvent if $\chi > 1/2$, and a good solvent if $\chi < 1/2$.

Flory–Huggins theory ignores the correlation between monomers due to the links
along the chain and assumes the calculation of the polymer arrangements is unaf-
fected by the interactions with the chains already placed (except by their “average
presence" as encapsulated in the volume fraction). This makes it an appropriate description of concentrated polymer solutions where such correlations can be ignored (since they are like a regular solution with the exception of chain identity). It is inappropriate for dilute solutions, where chain connectivity matters. Further, since the model ignores the possibility of concentration fluctuations, it is quantitatively inappropriate for overlap polymer solutions, where concentration fluctuations are large. The qualitative behaviour of semidilute solutions is however well captured by Flory–Huggins theory.

2.3.2 Concentration Fluctuations and Screening

It is possible to account for concentration fluctuations in the mean field provided such fluctuations are small or slowly varying (e.g. the small fluctuations of a melt, or the slow concentration variation at an interface). In the former case the free energy can be expanded in the concentration fluctuations, with the expansion coefficients fixed by appeal to the so called random phase approximation (RPA) [16, 45, 14]. In the square gradient approximation (SGA) [46, 47] a square gradient term accounts for the entropic restrictions caused by fluctuations, the coefficient of the square gradient coefficient is usually fixed by comparison of the small fluctuation limit of the SGA with the slowly varying limit of the RPA. We outline these developments in turn.

Free Energy Expansion

Suppose that a polymer solution exhibits small fluctuations $\delta \phi(r)$ at position $r$ about a uniform concentration $\phi_0$. The monomer volume fraction is then given by $\phi(r) = \phi_0 + \delta \phi(r)$ and we can expand the free energy as a functional Taylor expansion [31]:
\[ F[\phi_0 + \delta\phi(r)] = F[\phi_0] + \int_V dr \frac{\delta F}{\delta\phi(r)} \delta\phi(r) + \]
\[ + \frac{1}{2} \int\int_{V,V'} dr dr' \frac{\delta^2 F}{\delta\phi(r)\delta\phi(r')} \delta\phi(r)\delta\phi(r') + \ldots \]
\[ = F_0 + \frac{1}{2} \int\int_{V,V'} dr dr' \mathcal{G}(r,r')\delta\phi(r)\delta\phi(r') + \ldots \]

where \( F_0 \equiv F[\phi_0] \) is the (constant) free energy of the uniform state and \( \mathcal{G}(r,r') \equiv \delta^2 F/(\delta\phi(r)\delta\phi(r')) \) is a function which represents the susceptibility of the system to fluctuations (the neglected terms will contain higher order susceptibilities). Note that the linear terms in \( \delta\phi(r) \) vanish by symmetry.

If we express \( \delta\phi(r) \) as Fourier series then:

\[ \delta\phi(r) = \sum_q \delta\phi_q e^{iq \cdot r} \]

with Fourier coefficients \( \delta\phi_q = (1/V) \int_V \delta\phi(r)e^{-iq \cdot r} \) (\( q \) is the wavevector dual to the position \( r \)). Equation (2.17) becomes to second order in \( \delta\phi \):

\[ F = F_0 + \frac{1}{2} \sum_q S^{-1}(q)|\delta\phi_q|^2 \]

To evaluate the free energy we need an expression for \( S^{-1}(q) \), the Fourier coefficient which corresponds to \( \mathcal{G}(r,r') \). \( S^{-1}(q) \) can be calculated in the random phase approximation, as shown in the next section. First, however let us consider the meaning of \( S^{-1}(q) \) and why we expressed it as a reciprocal.

The probability of a fluctuation about the uniform state of size \( \delta\phi \) is given by

\[ p \propto e^{-\Delta F/T}, \]

where \( \Delta F \equiv F - F_0 \) is the free energy cost of a fluctuation. If we write\(^\text{ix} \)

\[ \Delta F = \sum_{q>0} S^{-1}(q)|\delta\phi_q|^2, \]

\( \Delta F \) is sum of independent modes and the

\(^\text{ix} \)So that the constraint \( \delta\phi_{-q} = \delta\phi_q^* \) is used to fix values for the remaining halfspace \( q < 0 \) (see §146 of [29]).
probability factors into a product of gaussian probabilities for each mode \( q \), given by \( p_q \propto e^{-\langle S^{-1}(q)|\delta \phi_q|^2 \rangle / T} \). The variance of each of these gaussians is:

\[
\langle |\delta \phi_q|^2 \rangle = \frac{S(q)}{T}
\]  

(2.20)

\( S(q) \) is thus proportional to the Fourier transform (FT) of the mean square fluctuation of mode \( q \), which is, in turn, the FT of the density–density correlation function: \( \Gamma(r - r') \equiv FT^{-1}[S(q/T)] = \langle \delta \phi(r)\delta \phi(r') \rangle \) (where \( FT^{-1} \) denotes an inverse Fourier transform).

**Random Phase Approximation**

The random phase approximation is a mean field scheme for the evaluation of the correlation function of a polymer solution. The average concentration fluctuation \( \langle \delta \phi(r) \rangle_u \) (where the subscript is to distinguish from the canonical average which would be zero) due to a small perturbing potential \( u(r) \) is linear in the perturbation:

\[
\langle \delta \phi(r) \rangle_u = -\int_V \Gamma(r - r')u(r') \, dr'
\]  

(2.21)

Where the minus sign reflects the fact that a positive disturbance causes a decrease in concentration. Fourier transforming both sides we have:

\[
\langle \delta \phi(q) \rangle_u = -\frac{1}{T}S(q)u(q)
\]  

(2.22)

If all interactions are ignored, then \( S(q) \) becomes \( S^0(q) \), the Fourier transform of the correlation function of a gas of ideal chains. We can then include the effect of interactions as a small perturbation about this ideal state. In the mean field these interactions are linear in \( \langle \delta \phi(q) \rangle_u \), which is a small quantity, we can thus write:
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\[
\langle \delta \phi(q) \rangle_u = -\frac{1}{T}S^0(q) [u(q) + k_{ni} \langle \delta \phi(q) \rangle_u]
\]

(2.23)

where \( k_{ni} = \delta u/\delta \phi(q) \) is a constant accounting for the contributions of the steric and Van der Waals nonideal interactions (hence the subscript), as approximated by a \( \chi \) parameter. Since the interaction potential is given by the functional derivative of the nonideal part of the free energy with respect to the monomer concentration, \( u = \delta f_{ni}/\delta \phi(q) \), its not hard to see that \( k_{ni} \) represents the nonideal compressibility of the polymer solution evaluated at the average concentration \( \phi_0 \) about which fluctuations occur:

\[
k_{ni} = -\frac{\partial^2 f_{FH}}{\partial \phi^2} \bigg|_{\phi=\phi_0} = -\frac{1}{1 - \phi_0} + 2\chi
\]

(2.24)

Equation (2.23) is a linear equation which we can solve for \( \langle \delta \phi(q) \rangle_u \). We find:

\[
\langle \delta \phi(q) \rangle_u = -\frac{1}{T} \left( \frac{1}{S^0(q)} + \frac{1}{1 - \phi_0} - 2\chi \right)^{-1} u(q)
\]

(2.25)

So that upon comparison with Equation (2.22) we see that:

\[
S^{-1}(q) = \frac{1}{S^0(q)} + \frac{1}{1 - \phi_0} - 2\chi
\]

(2.26)

\( S^0(q) \) is a well known function which takes the following form [17]:

\[
S^0(q) = \phi_0 N g_D(q^2 R_g^2)
\]

(2.27)

where \( g_D(x) = 2(e^{-x} - 1 + x)/x^2 \) is the Debye function [17] and \( R_g = (N/6)^{1/2}a \) is the radius of gyration of an ideal polymer (\( N g_D \) is the monomeric pair correlation function of such a polymer in \( q \) space).

Using Equations (2.19), (2.26) and (2.27) we can thus evaluate the free energy contribution of fluctuations in polymer concentration.
Square Gradient Approximation

An alternative method for the calculation of the free energy contribution due to fluctuations is provided by the square gradient approximation [46, 47]. If there were no fluctuations the free energy density of a solution at a point \( f(\phi(r)) \) would have the same functional form as the free energy of a homogeneous solution: \( f(\phi(r)) \equiv f_0(\phi(r)) \). For example, in a polymer solution \( f_0 \) would simply be given by the local version of the Flory-Huggins expression with \( \phi = \phi(r) \) in Equation (2.16). However if the composition is nonuniform because of fluctuations or interfaces, the free energy density at a point depends not only on the composition at the given position but also on the composition of the neighboring environment. Assuming \( \phi(r) \) is a well behaved function, Taylor’s theorem ensures that knowledge of all the derivatives of \( \phi(r_0) \) at a point \( r_0 \) is equivalent to knowledge of \( \phi(r) \) for all \( r \). Because of correlations the value of the free energy at a point depends on the concentration at all other points (in theory). It thus makes sense to expand \( f(\phi(r)) \) as Taylor series in \( \phi(r) \) and its gradients:

\[
f(\phi, \nabla \phi, \nabla^2 \phi, \ldots) = f_0(\phi) + [K_1(\phi) \cdot \nabla \phi + k_2(\phi)(\nabla \phi)^2/2 + \ldots] + [k_3(\phi)\nabla^2 \phi + \ldots] + \ldots \tag{2.28}
\]

Where \( f_0 \) is the reference free energy defined above and \( K_1, k_2, k_3 \) are unknown functions of \( \phi \) given by the derivatives of \( f \) with respect to the appropriate concentration gradient evaluated at the reference state. In the absence of a local source of anisotropy biasing the concentration gradients in a preferred direction, the free energy cannot depend on any particular direction of the concentration gradients, thus only the even powers of Equation (2.28) are nonzero. The volume integral of Equation (2.28) gives the free energy of the solution:

\[
F[\phi(r)] = \int_V [f_0(\phi) + k_2(\nabla \phi)^2/2 + k_3 \nabla^2 \phi + \ldots] dV \tag{2.29}
\]

\(^\text{e.g.:} \quad K_1(\phi) = (\partial f/\partial \nabla \phi)_0, \) which is the reason for the dependence on \( \phi. \)
By Green's first identity \( \int_V k_3 \nabla^2 \phi \, d\mathbf{r} = \int_S k_3 \nabla \phi \cdot d\mathbf{S} - \int_V dk_3 / d\phi (\nabla \phi)^2 \, d\mathbf{r} \), whose surface integral vanishes with an appropriate choice of enclosing boundary (e.g. the solution container). The free energy is thus, to second order in the gradient expansion:

\[
F[\phi(\mathbf{r})] = \int_V [f_0(\phi) + \mathcal{K}(\phi)(\nabla \phi)^2] \, d\mathbf{r} \tag{2.30}
\]

where \( \mathcal{K}(\phi) \equiv k_2(\phi)/2 - dk_3/d\phi \) is another unknown function of \( \phi \). If concentration fluctuations are slowly varying, Equation (2.30) is an accurate description of the free energy of a nonuniform system, since the most significant contribution to the energetic cost of fluctuations is accounted for by the square gradient terms (hence the name of the approximation). An example where the SGA is a good approximation is at the interface between two phases where the concentration slowly changes from the average concentration of one phase to that of the next.

However, since \( \mathcal{K}(\phi) \) is an unknown function of \( \phi \) Equation (2.30) is of limited practical value until this function is found somehow.

**Fixing the Value of \( \mathcal{K}(\phi) \)**

The SGA is valid for slowly varying fluctuations, whereas the free energy expansion discussed earlier applies for small fluctuations about a uniform state. We can thus expand the Equation (2.30) for small fluctuations and compare it with the slowly varying fluctuations limit of the free energy expansion. To find the latter we consider only the fluctuations which have a large wavelength with respect to the ideal chain state: \( qR_g \ll 1 \). In this limit the Debye function becomes: \( g_D(q^2R_g^2) = 1 - q^2R_g^2/3 \) and, recalling that \( R_g^2 = Na^2/6 \), Equation (2.26) becomes:

\[
S^{-1}(qR_g \ll 1) \simeq \frac{1}{N\phi_0} + \frac{1}{1 - \phi_0 - 2\chi} + \frac{a^2}{18\phi_0}q^2 \tag{2.31}
\]
and the free energy (2.19) is:

\[ F = F_0 + \frac{1}{2} \sum_{\mathbf{q}} \left( \frac{1}{N\phi_0} + \frac{1}{1 - \phi_0} - 2\chi + \frac{a^2}{18\phi_0} \mathbf{q}^2 \right) |\delta \phi_{\mathbf{q}}|^2 \tag{2.32} \]

Next we expand the square gradient free energy (2.30) to second order about the uniform state $\phi_0$:

\[ F[\phi_0 + \delta \phi(\mathbf{r})] = F_0 + \int_V \left[ \frac{1}{2} \left( \frac{d^2 f_{FH}}{d\phi^2} \right)_{\phi = \phi_0} \delta \phi(\mathbf{r})^2 + \mathbf{K}(\phi_0)(\nabla \delta \phi(\mathbf{r}))^2 \right] d\mathbf{r} \tag{2.33} \]

where $F_0 = \int_V f_{FH}(\phi_0) d\mathbf{r}$, the term linear in the fluctuation vanishes by symmetry as before and (see ch. IV of [15]):

\[ \left( \frac{d^2 f_{FH}}{d\phi^2} \right)_{\phi = \phi_0} = \frac{1}{N\phi_0} + \frac{1}{1 - \phi_0} - 2\chi = S^{-1}(0) \tag{2.34} \]

Expressed as a Fourier sum Equation (2.33) reads:

\[ F = F_0 + \frac{1}{2} \sum_{\mathbf{q}} \left( \frac{1}{N\phi_0} + \frac{1}{1 - \phi_0} - 2\chi + 2\mathbf{K}(\phi_0)\mathbf{q}^2 \right) |\delta \phi_{\mathbf{q}}|^2 \tag{2.35} \]

A comparison of the coefficient of the $\mathbf{q}^2$ term in Equations (2.35) and (2.31) yields:

\[ \mathbf{K}(\phi) = \frac{a^2}{36\phi} \tag{2.36} \]

where we have replaced the reference $\phi_0$ state with a general concentration $\phi$.

It is worth mentioning that a different coefficient is sometimes proposed arising from the high $\mathbf{q}$ limit of the Debye function, which yields a factor of 24 instead of 36 in the denominator of Equation (2.36) [16, 15, 48].
2.3. POLYMER SOLUTIONS

Screening in the Mean Field

Equation (2.33) can be simply recast as an expression for the variation of the free energy when a uniform state is perturbed by a fluctuation $\delta \phi$:

$$\delta F = \int_V \left[ (\nabla \delta \phi(r))^2 + \frac{1}{\xi^2} \delta \phi(r)^2 \right] dr$$

(2.37)

where $\xi^2 \equiv 2\chi(\phi)/(\partial f_{FH}/\partial \phi)$ defines a characteristic length $\xi$. Using Equations (2.36) and (2.34), we have:

$$\xi^2 = \frac{a^2}{18 \left( \frac{1}{N} + \frac{\phi}{1 - \phi} - 2\chi \phi \right)}$$

(2.38)

The null variation of Equation (2.37) yields a differential equation for the equilibrium fluctuations:

$$\nabla^2 \delta \phi(r) = \frac{1}{\xi^2} \delta \phi(r)$$

(2.39)

Equation (2.39) is mathematically identical to the Debye–Hückel equation (2.7) derived in Section 2.2.1. $\xi$ is thus a screening length, which, in the physical situation of a polymer solution, represents the scale over which concentration fluctuations are significant. Beyond this scale the fluctuations die away because of the randomizing effect of the interactions with other chains.

The similarity between the physics of polymers and of charged systems is striking. The interior of a concentrated polymer solution is analogous to a dilute electrolyte solution: if we take a monomer and look at its perturbation on other monomers, the effect dies off, with a decay (characterised by $\xi$ for very small perturbations), just like the potential in a salt solution falls over a Debye length. Similarly, a nonadsorbing polymer solution near a wall is analogous to a charged surface

\[\text{x1This means the polymer monomers are repelled upon contact with the surface.}\]
in an electrolyte: the reduction of entropy of the solution by the wall depletes the polymer concentration only within a characteristic distance (the "depletion zone"), just as the electrostatic influence of the wall is screened by the electrolyte ions.

**Depletion–Induced Attraction**

The depletion of a polymer by a surface implies that approaching surfaces, in contact with a polymer reservoir, will feel an "attraction" when the distance between them is such that their depletion zones overlap. This attraction is due to the imbalance of pressures between the region between the surfaces, which can accommodate no polymer because of the repulsive effect of the wall, and the reservoir solution exerting pressure outside them\(^{\text{xii}}\).

For separations much greater than a couple of depletion zones, the pressures will balance and no attraction will be felt. From a thermodynamic point of view the attraction is a result of the increase in the polymer entropy when the plates are collapsed together, since this increases the space which can be explored by the polymer.

Similar considerations apply to surfaces of different geometry (e.g. colloids in a polymer solution as mentioned in Section 2.1.5).

### 2.3.3 Scaling Approaches

Flory–Huggins (FH) theory, like any mean field theory, does not apply quantitatively where correlations between chains are significant. Dilute and semidilute polymer solutions are poorly described by the theory.

However, an intelligent application of scaling and renormalisation group (RG) approaches (originally developed in the context of classical phase transitions and

\(^{\text{xii}}\)Such force is analogous to the Casimir effect experienced by conducting plates in a vacuum [5, 49] or acoustic plates subjected to white noise [50].
critical phenomena [51]) to polymers has allowed an accurate description of these concentration regimes in polymer solutions, with excellent agreement with experiment [15, 14].

We will not review scaling or RG methods, whose qualitative content does not differ significantly from the basic Flory–Huggins picture which we will adopt in the model of Chapter 5. How the model might be modified by adopting such methods is discussed briefly in Chapter 8.

### 2.4 Dielectric Mixtures

In this section we discuss the electrostatic treatment of mixtures of substances with different electrical permittivities.

The situation is as follows: a substance with permittivity $\varepsilon_1$ contains dotted within it inclusions of permittivity $\varepsilon_2$ occupying a volume fraction $\phi$ and arranged homogeneously and isotropically. We could have, for example, oil droplets in a oil–water emulsion or air pockets in a porous material.

We want to know the electrostatic behaviour of such mixtures, that is their response to an applied field due a distribution of free charge.

An exact treatment of the problem would involve the solution of Maxwell’s equations for the system on a local scale and a subsequent averaging to obtain the bulk electrical behaviour (e.g. [52]). This is clearly a horrible task, even for simple cases. Mixtures are better tackled using effective medium approaches whereby reasonable approximations allow one to evaluate the effective permittivity of the mixture.

#### 2.4.1 Effective Permittivity of a Mixture

The effective medium approach treats dielectric mixtures as a single medium with an effective permittivity originating from the combined properties of the host and
the inclusions. This is possible if the electric field $\mathbf{E}$ and polarization vector $\mathbf{P}$ (and so the electric displacement: $\mathbf{D} \equiv \varepsilon_0 \mathbf{E} + \mathbf{P}$) are averaged over volumes large enough to contain many inclusions, so that they "see" a homogeneous and isotropic medium. Let the averaging volume $V$ be characterised by a radius $R$ and let the number concentration of inclusions be $n$. Averaging is thus possible only if:

$$R \gg n^{-1/3}$$  \hfill (2.40)

The constitutive relation of the mixture is then given by:

$$\langle \mathbf{D} \rangle = \varepsilon_e \langle \mathbf{E} \rangle \hfill (2.41)$$

which defines the effective permittivity $\varepsilon_e$. The averages $\langle \ldots \rangle$ denote here volume averages, so that $\langle \mathbf{D} \rangle = (1/V) \int_V \mathbf{D} \, d\mathbf{r}$ and the likewise for $\langle \mathbf{E} \rangle$, with integrals over the averaging volume $V$.

For a variety of particle shapes and permittivity, Equation (2.41) allows us to find how $\varepsilon_e$ depends on the properties of the mixture, namely the permittivity of the host and inclusions, and the shape of the latter. We will consider the case of a mean field description of spherical inclusions (reference [53] contains many other geometries and more sophisticated mixing approaches).

**Spherical Inclusions**

The simplest inclusions that can be considered are spheres of equal radius $a$ and permittivity $\varepsilon_2$. Let these occupy a volume fraction $\phi$ of the host medium, whose permittivity is $\varepsilon_1$.

We expect the effective permittivity to depend on the two dielectric constants and the concentration of spheres. The functional form of $\varepsilon_e$ can be derived to be (see Chapter 3 of [53]):
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\[
\varepsilon_e(\phi) = \varepsilon_1 \left( 1 - \frac{3K\phi}{1 + K\phi} \right) \tag{2.42}
\]

where \( K \) is the Clausius–Mossotti factor:

\[
K = \frac{\varepsilon_1 - \varepsilon_2}{2\varepsilon_1 + \varepsilon_2} \tag{2.43}
\]

Equation (2.42) is a recast of the Clausius–Mossotti equation of classical electromagnetism [53, 34] and is known as the Maxwell–Garnett equation. Its derivation is based on the assumption that the local field at each sphere is the superposition of the external field and the average polarisation field due to all the other spheres. Interestingly the low concentration limit of (2.42) can be derived independently of this assumption, as done e.g. in [54], and represents an “exact” limit, recovered by most other mixing approaches (see sect. 9.2 of [53]). It reads:

\[
\varepsilon_e(\phi) = \varepsilon_1 (1 - 3K\phi) \tag{2.44}
\]

2.5 Electrostatics of Inhomogeneous Dielectrics

In this section we further address the variational approach to electrostatics.

2.5.1 Poisson’s Equations for Inhomogeneous Dielectrics

We have seen how the permittivity of a mixture changes with its composition. Suppose now that, while uniform and isotropic on a local scale, the composition \( \phi \) is not uniform over a large region of a mixture, but is instead a function of position: \( \phi = \phi(\mathbf{r}) \). The effective permittivity is then itself a function of position: \( \varepsilon_e = \varepsilon_e(\mathbf{r}) \). The constitutive relation for this kind of mixture is given by:
\[ \mathbf{D}(\mathbf{r}) = \epsilon_e(\mathbf{r})\mathbf{E}(\mathbf{r}) \]  

(2.45)

and the Maxwell equations describing this physical situation are:

\[ \nabla \cdot \mathbf{D} = \rho \]  

\[ (2.46) \]

\[ \nabla \times \mathbf{E} = 0 \implies \mathbf{E} = -\nabla V \]  

\[ (2.47) \]

where \( \rho(\mathbf{r}) \) is the density distribution of free charge. Substituting Equation (2.45) for \( \mathbf{D} \) and (2.47) into (2.46) we have Poisson's equation for inhomogeneous media:

\[ \nabla \cdot (\epsilon_e(\mathbf{r})\nabla V) = -\rho \]  

\[ (2.48) \]

where only the dependence on position of \( \epsilon_e \) has been made explicit for clarity (we will adopt this convention until the end of this section). Using (2.48) and appropriate boundary conditions, it is possible to describe the electrostatics of inhomogeneous mixtures, provided the functional form of the composition variation is known, since this implies a knowledge of the spatial variation of the permittivity. In Chapter 4 we will combine this approach with the Gouy–Chapman model to provide a self-consistent expression for \( \phi(\mathbf{r}) \) in a system comprising a mixture of electrolyte ("dielectrically" identical to water) and low permittivity spherical inclusions.

Note, that while the above equations describe inhomogeneous materials, they do not hold for locally anisotropic materials, where the permittivity is a different constant in different directions (a tensor) or nonlinear materials, where the polarisation of the material does not change linearly with the applied field.

### 2.5.2 Variational Formulation

It is sometimes convenient to formulate electrostatics variationally, so that Maxwell's equations for electrostatics are seen to arise from the requirement that an elec-
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trostatic action be stationary. This is useful, for example, if one wants to use variational methods to derive the mean field equations for a charged system (as we shall see in more detail in Chapters 4 and 5).

General Electrostatic Action

Our plan is to recover Equations (2.46) and (2.47) as stationary variations of an electrostatic action. This takes the following form:

\[
\mathcal{A}[V, D] = \int_{V'} \left[ \rho V + D \cdot \nabla V + \frac{D^2}{2\varepsilon(r)} \right] \, dr \tag{2.49}
\]

Equation (2.49) has dimensions of energy and is the electrostatic analogue of a Hamiltonian action in mechanics (with the sign reversed) [34]. Performing the independent variations \( V \rightarrow V + \delta V \) and \( D \rightarrow D + \delta D \) on (2.49), the stationarity condition is:

\[
\delta \mathcal{A} = \int_{V'} \left[ \rho \delta V + \delta D \cdot \left( \nabla V + \frac{D}{\varepsilon(r)} \right) + D \cdot \nabla \delta V \right] \, dr = 0 \tag{2.50}
\]

Since the divergence operator is linear, we have the identity \( D \cdot \nabla \delta V = \nabla \cdot (D \delta V) - \delta V \nabla \cdot D \). We can then use the divergence theorem to evaluate \( \int_{V'} \nabla \cdot (\delta V D) \, dr = \int_S \delta V D \, dS \) = 0 \text{ xiii.} Equation (2.50) then becomes:

\[
\delta \mathcal{A} = \int_{V'} \left[ \delta V \left( \rho - \nabla \cdot D \right) + \delta D \cdot \left( \nabla V + \frac{D}{\varepsilon(r)} \right) \right] \, dr = 0 \tag{2.51}
\]

To satisfy relation (2.51), the contents of the two brackets Equation (2.51) need to be independently null. This implies Equations (2.46) and (2.47), if we recall the constitutive relation (2.45). Substituting these into Equation (2.49) and integrating by parts as above, yields the value of the electrostatic energy for the

\text{xiii} The potential is set to zero at infinity, and since the volume of integration includes all of space, \( \delta V = 0 \) on the enclosing surface (at infinity).
fields $\mathbf{D}$, $\rho$ and $V$ which are constrained to obey Maxwell’s equations. This is indeed the total electrostatic energy of the system:

$$U_{el} = \int_{V'} \frac{1}{2} \varepsilon_e(r)(\nabla V)^2 d\mathbf{r} = \int_{V'} \frac{1}{2} \rho V d\mathbf{r}$$

(2.52)

The Action as a Functional of the Potential

The electric field is conservative, $\mathbf{E} = -\nabla V$, and if we substitute this into Equation (2.49), the action becomes a functional of the electrostatic potential only:

$$A[V] = \int_{V'} \left[ \rho V - \frac{1}{2} \varepsilon_e(r)(\nabla V)^2 \right] d\mathbf{r}$$

(2.53)

Performing the variation $\delta A/\delta V = 0$ then yields Poisson’s equation (2.48). If $V_0$ is a solution to Poisson’s equation, $A[V_0]$ is identical to the electrostatic energy of the system (2.52) (as can be seen, once more, by substitution and integration by parts). We note in passing that $A[V] \leq A[V_0] \equiv U_{el}$ for an arbitrary potential $V$: to say, the true energy $U_{el}$ of an electrostatic system is the maximum possible value of (2.53)\textsuperscript{xiv}.

The functional (2.53) is convenient when problems involving electrostatic contributions to the energy are formulated variationally. An alternative would be to use (2.52) with the differential constraint that $V$ and $\rho$ obey Poisson’s equation, which is a more cumbersome analytic approach [55]. To avoid such complications, we will employ the variational formulation just presented when developing a mean field description of dielectric solutes between charged surfaces, presented in Chapters 4 and 5.

\textsuperscript{xiv}The alternative functional found assuming $\nabla \cdot \mathbf{D} = \rho$ instead bounds the true energy from above [34], but is less useful for the purpose of this thesis.
2.6 Current Issues in Charged Soft Matter

The above survey completes the theoretical tools used later in the thesis. In this section we review recent developments, which are interesting and close to our own work to, but not explicitly built on in subsequent chapters.

To begin with, shall first describe how a growing number theoretical investigations have been recently exploring the limits of the Debye–Hückel/Gouy–Chapman descriptions, with particular emphasis on when the underlying mean field approximations no longer hold and need to be replaced by more sophisticated treatments. This research has been recently made relevant by experiments on biologically inspired systems, whose large charge and complex ionic makeup provide ample scope for experimentally observable violations of "classical" electrostatic behaviour. Next we shall introduce investigations on dielectric contrast driven effects, a subject very close to our work. Finally, we will consider other work concerned with the interplay of electrostatic and other effects in determining the structure and interaction of complex systems, again with biological systems providing a guide to where the interesting behaviour is to be experimentally observed.

2.6.1 Beyond Mean Field Theory

As mentioned in Section 2.2.1, mean field theories of charged systems are a good approximation for small electrostatic correlations between ions. Theoretically we should thus expect a breakdown of the mean field description for systems where such correlations cannot be ignored. The correlations stem from electrostatic interactions between ions. If the latter are stronger than thermal agitation the system will tend to resume its energetically preferred electroneutral state, a situation which can be induced by confinement (crowding), as when concentrated salt solutions "salt out", or by lowering the temperature.
Simple though the basic physics may be, extending the mean field description is not a trivial task, because of the long range nature of the electrostatic interaction. Reference [30] provides a good overview of the traditional extensions of the Debye–Hückel description for concentrated electrolytes and reference [39] will give the reader a detailed insight into the current progress in the electrostatics of soft matter systems.

2.6.2 Counterion Condensation and Ion Correlation Effects

Progress beyond the standard description of macroions made significant advances when Oosawa [56] and Manning [57] independently developed the concept of counterion condensation. This involves a geometry–dependent collapse of counterions onto their parent surface when its electrostatic attraction dominates the randomising effect of entropy. When viewed from afar, a macroion surface, whose counterions are condensed, bears a renormalised charge (this depends on geometry: e.g. flat surfaces always condense the ions, thus showing zero renormalised charge) which reduces the effective interaction between macroions. Though developed within the mean field the description of isolated polyelectrolytes in a saltless solution, Oosawa–Manning condensation is not an entirely mean field effect (the "ion condensate" is strongly interacting) and is now believed to be quite real, with substantial experimental support. It remains however uncertain exactly why it happens in real systems (see the contribution by Williams in [39]).

Counterion condensation paved the way to the analysis of ion correlation attractions. It has been long known that charged biological macromolecules can be wrapped and packed very efficiently, despite bearing net charges of the same sign. Specifically, certain biological salts (spermidine, for example) can cause DNA chains to attract [23]. The possibility that such counterintuitive behaviour could be due to the ion correlations neglected by mean field theory, despite the pioneering theoretical investigations of Oosawa [56] and simulations by the Guld-
brand et al. [58], has only recently begun to be accepted as feasible, with several experimental investigations supporting this hypothesis [23, 39]. It is beyond the scope of this short review to discuss the many mechanisms proposed to explain such effects, which still represent a debated subject. Great progress has been made in recent years [39], and it appears, from what we understand of these recent developments, that the debate now focuses on the applicability of proposed mechanisms to particular experimental situations. Experiments which can clearly filter out any effects which might affect the ion correlation forces are hard to perform, but are definitely possible. For example, in a recent experiment by Angelini et al. [59], the attraction between actin filaments is observed to arise from the formation of "frozen charge density wave" of counterions; the shape of this wave is such as to interlock with the actin filaments and causes them to collapse upon it.

Validity Criterion for Planar Surfaces

In the case of a planar surface, a dimensionless parameter can be derived (see the contribution by Netz and Moreira in [39]), which expresses the strength of the electrostatic interaction at the surface, allowing to establish if mean field theory is applicable. The parameter is found by comparing the relative magnitude of the 2D and 3D electrostatic interaction between charges in thermal units. We can assign a lengthscale, Bjerrum length $l_B$ (defined in Section 2.2.1) multiplied by the ion valency $z_i$, to the 3D interaction; similarly, for the 2D case, the relevant scale is the so called Gouy–Chapman length $\Lambda \equiv 1/2\pi z_i \sigma l_B$. The ratio of the two scales is the coupling parameter $\Xi \equiv 2\pi l_B^2 z_i^3 \sigma$, such that if $\Xi < 1$ the counterions will form a gas above the surface, as correctly described by a mean field model, and if $\Xi > 1$ the condensation of the ions at the surface is favoured.

The coupling parameter depends on the ion valency and the surface charge, $\Xi \simeq z_i^3 \sigma$. These same conditions are associated with the arisal of counterintuitive effects caused by ion correlations. As we saw in the previous section, other
effects may often swamp or confuse the contribution of correlation induced forces. Nevertheless, if we are sure that correlation forces might be triggered, a “safe use” of mean field means avoiding highly charged surfaces and multivalent ions.

2.6.3 Effects of Electrical Polarisation

The Effect of Dielectric Contrast

Another interesting electrostatic effect to recently be confronted by the “soft” community is the fact that polarisation charges at dielectric interfaces are also the source of important interactions. Such considerations are at the core of this thesis. Yet again, the interest in such matters has a “biological muse”: the make-up of living organisms consists largely of fatty, hydrocarbon based molecules, such as lipids and protein base groups immersed in water. The simple-minded physicist, adopting a coarse grained viewpoint, sees a microscopic electrostatic lab where biological molecules and membranes are insulators, sometimes charged at the surface, and immersed in an easily polarised (and conducting) aqueous medium.

This point of view is not new and the continuum description of biological molecules can be found in the same paper by Perutz [7] that was quoted in the introduction. In it he reports a suggestion by Kauzmann to explain why electrolyte ions do not penetrate closer than a critical distance to a protein backbone: treating proteins as dielectric lumps of low permittivity, the effect is seen to be a result of “image dipole” repulsion which the protein surface exerts on the ions. The above considerations have recently been revived by the soft matter community since they are relevant to membranes, both biological and artificial, and their interaction with charged biological molecules. Schmidt et al. [60], for example, have examined the possible partitioning of counterions from their parent protein when this becomes immersed, for biological reasons, in a membrane. Similarly to the Perutz–Kauzmann problem, they propose that the ions will either prefer to re-
side in the high dielectric constant water and avoid, for energetic reasons, the low permittivity membrane interior, or, alternatively, by shielding themselves with a water shell, will manage to penetrate the membrane and keep in the proximity of the mother protein. A similar problem has been considered by Netz [61] when considering the interaction of charges with and across dielectric slabs within a Debye–Hückel framework. Many other interesting investigations on this subject can be found in the literature, such as those on fluctuation induced interactions in the presence of dielectric discontinuities [62, 63].

**Coupling of Dispersion and Electrostatic Forces**

Another interesting application of “dielectric effects” is found in a paper by Boström et al. [64]. Here the authors challenge the correctness of DLVO theory at physiological concentrations because of the non-negligible effect of dispersion and image forces exerted by the surfaces on the ions. The spirit of this challenge, which couples electrostatics with other physical effects, is very close to our own: in Chapters 4 and 5 we will show how dielectrics (which are not ions in our case) present between charged surfaces affect their interactions.

**2.6.4 Charged Polymers**

Finally, we mention, for the sake of completeness, another very important charged system: charged polymers. These come in three main varieties: polyelectrolytes, bearing only, or predominantly, one type of charge (positive or negative); polyampholytes, which carry alternating positive and negative charges; and ionomers, polyelectrolytes with groups which may or may not be ionised.

Charged polymers exhibit rich and complex behaviour: they are easily soluble in water, can be very stiff, and can tune their interactions in response to external changes (such as the salt induced attractions already discussed). Polyelectrolytes are the best understood charged polymers. The current description combines
polymer physics and electrostatics and is reasonably successful (see Joanny's contribution to [39] or [48]), except for the non-classical effects described in Section 2.6.2. Current interest in charged polymers has shifted from the study of structural conformations of a single chain, to that of solution properties (see the contribution by Williams to [39]); the adsorption at surfaces neutral [65] or charged [66]; interactions between chains (Section 2.6.2), between surfaces in a charged polymer solution [67, 68] and almost any other interesting combination. Charged polymers are also incorporated in lamellar phases [23], as mentioned in the introduction and as we shall see in Chapter 3.

The importance of charged polymers and their interactions is again made obvious by biology: DNA can be thought of as a highly charged polymer and the clever ways Nature has found to pack it, wrap it, unwrap it etc. to fit its functional purposes are intriguing to present day researchers.
Chapter 3

Relevant Experiments

In this chapter we review a selection of interesting studies which provide the experimental justification (a priori and a posteriori!) for the theoretical description developed in the following chapters.

Recall the purpose of our work is to investigate the effect of surface fields on the distribution of nearby neutral molecules in solution and the consequent modification of surface forces by this effect. The different experimental situations described below thus have one common feature: charged surfaces and neutral solutes (usually in an electrolytic solution).

In addition to providing motivation for our work, the experiments described below also demonstrate the feasibility of future experiments which could be performed to test the soundness of our hypothesis and its consequences.

We will divide the experimental systems according to the average curvature of their surface, so that we will first look at systems containing flat surfaces (lamellar phases) and then those which contain curved ones. Where necessary, some introductory remarks on the systems will be made.

The chapter is concluded by a brief mention of other interesting experiments on such systems, which we do not describe in detail as they are further removed from our study.
Flat Surfaces

3.1 Polymer-doped Lamellar Phases

A simple instance of charged surfaces sandwiching a polymer solution is that of surfactant lamellar phases "doped" with polymer\(^1\).

Such composite systems (whose existence does not require, in general, the charged surfaces and neutral surfactants we are interested in) were postulated by De Gennes \[71\] and realised by Kekicheff et al. \[72\]. Only recently, however, have lamellar–polymer mixtures been studied in greater experimental detail (see \[73\]) and only a handful of thorough theoretical analyses can be found on the subject \[74, 69, 75, 76, 77\].

**General Features**

A lamellar phase is a periodic stack of bilayers (see Fig. 6.1 in Chapter 6): a smectic liquid crystal whose order parameter is the average distance between the bilayers. We say average since the bilayers fluctuate both along the direction normal to their surface (compression mode) and, to a greater extent, they undulate about their average separation because of thermal fluctuations.

The behaviour of lamellar phases is governed by the forces between the bilayers. One important force between bilayers is due to the aforementioned undulation which causes different bilayers to bump into each other causing a repulsion known as Helfrich interaction. Further, like all surfaces in soft matter, bilayers experience attractive dispersion forces, and if they are charged, electrostatic interactions, which are usually repulsive. At close contact other forces have been shown to arise for charged bilayers. These are due to the hydration of the surface charges and are known as hydration forces.

\(^1\)Some investigators use this denomination to indicate only smectics whose bilayers contain polymers. Others \[69, 70\] use it more broadly, in a sense that we will soon explain.
3.1. POLYMER-DOPED LAMELLAR PHASES

A DLVO like approach can be adopted to describe lamellar interactions in terms of effective potentials. This approach often works well on a qualitative basis, but can be flawed because of unaccounted couplings between the various forces at play.

Independent of the method used to describe the lamellar phases, the presence of attractive and repulsive interactions between the bilayers can often cause them to phase separate. The same effect can be induced by the addition of polymer in doped lamellar phases (as for colloid–polymer mixtures).

Embedded, Adsorbing and Nonadsorbing Polymers

The polymers doping lamellar phases have been observed at different locations within a lamellar phase, depending on the polymer solubility in the solvent. The more soluble polymers have been deduced to reside in the solvent between bilayers (as in the experiments described in Section 3.1.1), with those possessing some affinity to the bilayer surface, being partially adsorbed to it (see Section 3.1.3). Surfactant–like polymers, poorly soluble in the solvent between bilayers, have been observed to be embedded in the bilayer [78, 79].

The mechanism causing polymer affinity to the bilayer and the consequent partial adsorption, is not clearly understood. One method used to investigate polymer–bilayer interactions is to look for perturbations in the aggregation concentration of polymer–surfactant solutions\(^{\text{ii}}\), which is reduced in the presence of polymer [21, 22]. However, the interaction between polymer and single surfactants may be different from that between polymers and surfactant bilayers, so that aggregation at the micellar level may not necessarily entail polymer adsorption onto bilayers.

\(^{\text{ii}}\)This is not generally identical to the critical micelle concentration (CMC) of surfactants, since the aggregates consist of complexes of polymers and surfactants.
Polymer Doped Charged Smectics

Bilayers can contain a certain density of charged surfactants. Such surface charge can be brought about artificially, but natural examples of charged bilayers abound (e.g. the lipid bilayers that make up cells).

Experiments have been recently carried out which mix charged lamellar phases and water soluble polymers. The latter can be charged or uncharged [73].

Our account of such experiments will be divided according to the presence or lack affinity to the bilayer. We do this because the possibility of polymer adsorption, i.e. of an attractive interaction with the surface, complicates the theoretical description of lamellar polymer mixtures.

3.1.1 Charged Smectics and Uncharged Nonadsorbing Polymers

CpCl/Hexanol/PVP/Water(brine)

An extensive study of a charged lamellar phase mixed with a nonadsorbing polymer has been carried out by Ligoure's group from Montpellier. They used lamellar phases whose bilayers consisted of a mixture of the cationic surfactant cetylpyridinium chloride (CpCl) and hexanol. These were formed in an aqueous salt solution (brine) in which the water soluble polymer polyvinylpyrrolidone (PVP) was dissolved. PVP is believed not to interact with cationic surfactants such as CpCl [80]. The effect of PVP on the critical micellar concentration (CMC) of a CpCl/Hexanol solution was checked by conductivity experiments [81]. A slight reduction in the CMC was found, independent of the presence of hexanol, and deemed insignificant by the authors. Such experiments seem to suggest that the polymer does not adsorb onto the bilayer; this belief is corroborated by the independence of the bilayer thickness of the amount of polymer [82].
3.1. POLYMER–DOPED LAMELLAR PHASES

All experiments were carried out for polymer concentrations above the estimated overlap concentration for PVP in brine; and all the parameters except the one under study were held fixed in the experiment. In a preliminary study [82], the progressive addition of salt (from 0 to 0.22 M) was found, in the presence of PVP, to induce a phase transition to two coexisting lamellar phases of different smectic periods (lamellar–lamellar phase separation); adding the same amount of salt to a polymer–free solution produced no such transition. It was inferred that a polymer–induced "attraction" (of sufficient magnitude to diminish the electrostatic repulsion between bilayers, when this was sufficiently screened by salt) was responsible for the transition. The "softening" of the layer repulsion was also estimated from a reduction of the bilayer compressional modulus, as inferred from the Caillé theory of scattering by smectics (see [82] and references therein), seeming to confirm the idea of an attraction caused by the polymer.

Later studies by the same authors extended the above investigation. It was shown [75] that for a pure water system (unscreened), the addition of PVP had no effect on the phase behaviour for the membrane fractions under study, whilst a progressive addition of salt induced a lamellar–lamellar phase separation at \( \sim 0.1 \text{ M} \). A further increase in the amount of salt caused an increased separation and sharpening of the Bragg peaks corresponding to the coexisting phases until \( \sim 0.2 \text{ M} \), where only one peak was observed corresponding to a smaller lamellar pitch than the initial salt–free one. This was interpreted as indicating the coexistence of a lamellar phase and an isotropic solution of surfactant micelles and polymer. In [83] the effect of a reduction of surface charge density was studied using mixed surfactants, yielding the same qualitative behaviour as the increase in salt concentration described above: as the area per surface charge \( \Sigma \) is increased (surface charge density falls) a lamellar–lamellar phase separation is observed at \( \Sigma \sim 320 \text{ Å}^2 \). Reference [84] extends the number of "transition inducing" parameters by studying the effect of reducing the amount of solvent and the amount of oil in the lamellar–polymer system.
3.1.2 Probably Nonadsorbing Cases

SDS/Hexanol/PEG/Water

Javierre et al. [85] from Bordeaux have studied a system whose lamellar bilayers consisted of the anionic surfactant sodium dodecyl sulfate (SDS), with hexanol as a cosurfactant, and mixed with an aqueous solution of the uncharged polymer polyethylene glycol (PEG).

Even though SDS/hexanol and PEG show associative behaviour at the micellar level, it has been found that mixed SDS/alcohol micelles interact less favourably with PEG the shorter the alcohol chain [86]. Further, Javierre et al. found no evidence (from the bilayer swelling laws) of any change in bilayer thickness upon addition of polymer when studying single phase samples in the polymer concentration range 20 - 165g/l. While this is not conclusive evidence that the polymer does not absorb to the lamellar bilayer, it is certainly evidence that the adsorption is not very significant, especially when compared with the results for the same system with octanol as the cosurfactant (see Section 3.1.3).

In their paper the authors present the effect of addition of PEG to the SDS/Hexanol lamellar phase with bilayers of fixed composition. They probe the phase structure by X-ray scattering and, from this, construct a full density-density phase diagram (Fig. 3.1).

From the phase diagram in Fig. 3.1 the authors notice the following: the addition of polymer induces at intermediate polymer and bilayer concentrations a lamellar-lamellar (LαLα) closed loop coexistence region; surrounding this is a region where a single lamellar phase (Lα) exists which can solubilise polymer up to \( \sim 175g/l \) (16% of the water can be replaced by polymer); the latter region narrows down with increasing polymer concentration (the swelling is reduced) giving way on its left boundary to a coexistence between a lamellar phase and an isotropic surfactant/polymer solution (LαL). The right hand boundary between the Lα phase and the LαL coexistence is not visibly affected by the polymer: the phase
3.1. POLYMER–DOPED LAMELLAR PHASES

is parallel to the polymer axis.

Another important observation is that while the $L_\alpha L$ coexistence (on the left) is immediately affected by the polymer, the $L_\alpha L_\alpha$ coexistence only occurs above the overlap concentration of the polymer solution ($\sim 35\text{g/l}$) and for lamellar spacings of order of the polymer radius of gyration.

Finally, the authors show evidence for the possible existence of a critical point where the $L_\alpha L_\alpha$ transition is second order. Plotting the smectic period (the order parameter) versus inverse membrane fraction (the phase transition inducing "field") it is possible to evidence the continuous nature of the transition for the polymer concentration fixed at $C_p = 75\text{g/l}$ (Fig. 3.2a), as opposed to the discontinuous behaviour for $C_p = 100\text{g/l}$ (Fig. 3.2b).

Further evidence that $C_p = 75\text{g/l}$ may be in the neighborhood of a critical point in the phase diagram is provided by the broadening of the Bragg peak in the scattering patterns upon addition of polymer for a fixed membrane composition (also on the phase boundary). The broadening, as the authors note, could be due to a
Figure 3.2: The swelling behaviour for $C_p = 75\text{g/l}$ (a) and $C_p = 100\text{g/l}$ (b). (The figure is from reference [85]). $d$ denotes the smectic period and $1/\Phi_M$ the inverse membrane fraction. Notice how the difference in smectic periods in (a) appears to vanish in a continuous manner as $1/\Phi_M$ is increased.

vanishing (or almost vanishing) layer compression modulus in the neighborhood of the critical point.

**SDS/Pentanol/PEG/Water**

The almost identical SDS/Pentanol/PEG has been studied by Freyssingeas et al. [87]. We shall not discuss the details of their study, because they looked at dilute PEG solutions, which our model (Model II of Chapter 5) cannot describe. According to the reportedly decreasing affinity between micelles and PEG with decreasing alcohol chain length [86], we expect this system to be nonadsorbing.

Freyssingeas et al. used a surface force apparatus to measure the force between surfaces, with doped lamellar phase sandwiched in between, as a function of distance. This allowed them to evaluate the decrease in the compressibility modulus of a lamellar phase with increasing polymer content. This behaviour is similar to that of the other doped smectics described in this chapter.
3.1. POLYMER-DOPED LAMELLAR PHASES

Other Systems

A range of other experiments have been carried out where nonadsorbing polymers have been mixed with charged lamellar phases. The vast majority of the interesting work is included in the review by Kötz and Kosmella [73]. The few existing water soluble polymers are usually employed in these experiments, most commonly PEG and polyacrylamide (PAM), combined with lamellar phases from a variety of common surfactants with or without added salt.

All we want to say here is that similar effects on the phase behaviour as reported above were reported by the investigators: changes in phase boundaries and reduced compressibility modulus.

3.1.3 Charged Smectics and Uncharged Polymers with Affinity Bilayer

SDS/Octanol/PEG/Water

In another study by Ficheux et al. [70, 77], the Bordeaux group looked at SDS/Octanol bilayers in aqueous PEG solutions. SDS/Octanol and PEG show stronger associative behaviour at the micellar level than hexanol and pentanol because of the longer hydrocarbon chain of octanol [86]; this is the reason why the polymer is considered adsorbing and included in this section.

As for the hexanol based system, a full phase diagram at fixed temperature and membrane composition was also obtained for this system, as shown in Fig. 3.3. Qualitatively, the same broad features can be observed as for the hexanol phase diagram: $L_\alpha L_\alpha$ coexistence at intermediate concentrations, surrounded by a doped lamellar phase which can solubilise polymer; reduced swelling of the lamellar phase (greater extent of “left hand side” $L_\alpha L$ coexistence). However, as Javierre et al. notice [85], the quantitative nature of these effects is different depending on the alcohol cosurfactant used. The octanol based system displays a larger $L_\alpha L_\alpha$
region than one with hexanol; in addition, as much as 50% of the water in the $L_\alpha$ phase ($C_p = 500g/l$) can replaced by polymer (as opposed to 16% for hexanol).

As for hexanol, the $L_\alpha L$ coexistence (on the left) appears immediately affected by the polymer but the $L_\alpha L_\alpha$ bound behaviour only occurs above a certain polymer concentration close to the the overlap concentration of the polymer solution, $C_p^* = 35g/l$. Notice that for hexanol the $L_\alpha L_\alpha$ coexistence appears above $C_p^*$, at $C_p \sim 50g/l$ and above a membrane fraction $\phi_m \sim 0.4$, whilst for octanol it appears below $C_p^*$, at $C_p \sim 5g/l$ and above a membrane fraction $\phi_m \sim 0.3$ (corresponding to a spacing comparable with the radius of gyration of the polymer coil) [85].

As in the previous studies, evidence from X-ray and neutron scattering [70, 77] seems to confirm the suspicion that the polymer reduces the repulsive interaction between bilayers. The compressibility modulus of the bilayers in a single phase lamellar phase was measured in different ways and shown to be reduced with respect to the expectations for electrostatically stabilised lamellar phase. Looking for a vanishing of the splitting between Bragg peaks, it was also possible for Ficheux et al. to estimate the two critical points of the closed–loop $L_\alpha L_\alpha$ region:
3.1. POLYMER–DOPED LAMELLAR PHASES

\((\phi_m \sim 0.32; C_p \sim 0.038)\) on the left and \((\phi_m \sim 0.58; C_p \sim 0.15)\) on the right. This estimate of the location of the left hand critical point was confirmed by a more thorough study [77] which mapped out the values of the Caillé exponent \((\eta \propto 1/\sqrt{B})\), where \(B\) is the compressibility) on the phase diagram of Fig. 3.3 and found it to diverge around \(\phi_m \sim 0.32; C_p \sim 0.038\) (so that \(B = 0\) in its neighborhood).

Finally, we report that Ficheux et al. [70] found that the classical swelling law was obeyed in the single phase regions of the phase diagram. However, addition of polymer affected the swelling of polymer–containing lamellar phase: plotting the smectic period against the inverse membrane fraction yielded straight lines of decreasing slopes. The authors proposed this could be explained either by penetration of the polymer in the bilayers or by a modification of the surfactant area per head group due to interference at the surface by adsorbed polymer.

Other Systems

The above adsorbing system has been discussed here in detail since it is an extensive study for which phase diagrams have been obtained. Other experiments have been carried out with adsorbing polymer solutions (usually with PEG as the polymer). As for the nonadsorbing polymers, a brief description of the experiments is included in the review by Kötz and Kosmella [73], and we shall not dwell on the details of the observations here.

We would only like to mention that Ficheux et al. [88], using conductivity measurements, found evidence supporting a strong interaction between PEG and AOT at the micellar level, in contrast to results with PAM/AOT. Further, their plots of the dilution law are compatible, within experimental uncertainty, with the conjecture that polymers do not penetrate inside the bilayer. This supports the picture of an adsorbing polymer forming a layer on the surface.
3.2 Mixtures of Charged Colloids and Uncharged Depletants

We now turn to systems whose charged surfaces are curved. These are treated separately since the curvature of their constituents can potentially complicate the behaviour of charged systems in many ways, whilst the lamellar phases are a good approximation to a one dimensional crystal of flat bilayers, as we shall see in Chapter 6.1. We will briefly discuss the complications introduced by curvature in Section 8.

In this section only mixtures of charged colloids and wormlike micelles are described in any detail. On one hand this is because they are the only system we are aware of which combines charged surfaces and polymer like molecules with a large amount polarisable material (the oily core of the micelles). On the other we do this for “historical” reasons, since it is the strange happenings in this system which provided the inspiration for this thesis.

3.2.1 Charged Colloids and Surfactant Micelles

**IDC Latex Particles and \( C_{16}E_{6} \)**

L. Galloway [89] studied an interesting system combining charged polystyrene colloids mixed with surfactant micelles formed by the nonionic surfactant \( C_{16}E_{6} \). In sufficient concentrations, \( C_{16}E_{6} \) assembles into wormlike micelles which behave similarly to polymers in many respects. The differences between the micelles and polymers are a consequence of self–assembly. Micelles differ from from polymers structurally: they are made not of chemically identical monomeric groups, but of aggregated surfactants, whose relatively long hydrocarbon chains make them
“chunkier” than the average synthetic polymer. In addition, the micelles are not the only surfactant solute, but exist in equilibrium with a solution of surfactants. As the concentration is increased the micelles grow in size. The growth is a statistical process, so that micelles exist in a distribution of lengths: they are polydisperse.

The study [89] was pursued to compare the behaviour of such systems to the well understood colloid–polymer mixtures, and see how far the analogy between the two can be pushed.

In a dilute colloid polymer mixture, the polymer causes an attractive contribution dependent on the polymer concentration [20]. Charge on the colloid and its screening by salt introduce a repulsive interaction. With these considerations in mind, the phase behaviour of sterically stabilised uncharged colloids (where the effect of charge was eliminated by PEO coating) and of charged colloids with or without salt was studied as the concentration of $C_{16}E_6$ was increased. The phase behaviour was measured for colloids of three different radii: 175, 105 and 70nm.

In the sterically stabilised case increasing the concentration of surfactant caused the colloidal fluid at low concentrations to phase separate into colloid rich ("liquid") and colloid poor ("gas") phases. At even higher concentrations the attractions were strong enough to cause the system to gelate.

For the charged colloids with added salt, the behaviour was similar to the sterically stabilised system with the same succession of phases, except at low surfactant concentrations where an unexplained instability against aggregation was observed (Fig. 3.4a). Apart from this, wormlike micelles and polymers have the same effect on colloids. Even despite any specific differences in depletion details, the experiments confirm that high concentrations of surfactant induce colloidal phase separation.

More surprising results were found in the study with no salt added. In this case the expectation is for the system to be electrostatically stabilised against depletion, given the large values of the screening lengths, as found by conductivity
Figure 3.4: Phase behaviour of Colloid–Micelle mixtures with (a) and without (b) added salt for 70, 105 and 175nm radius colloids (top to bottom). The experiments with added salt were performed with 0.01 volume fraction of polymer. Notice that appearance of phase separation of salt–less samples of 70nm colloids at surfactant concentrations similar to the case with added salt. Considering the electrostatic interactions on a salt–less sample are expected to be poorly screened, this is a surprising result, as discussed in the text. (The diagrams are reproduced from [89]).
measurements: $\lambda \sim 60\text{nm}$ for 175 and 70nm particles and $\sim 40\text{nm}$ for the 105nm ones. The phase behaviour in this case, is shown in Fig. 3.4b. No instability was observed at low concentrations of surfactant in this case, a likely consequence of the electrostatic stabilisation.

As the concentration of C$_{16}$E$_6$ is increased the fluid again separates into colloid rich and colloid poor phases, which this time are crystal–fluid or gel–gas coexistences. The liquid–gas coexistence is suppressed. When compared to the phase behaviour with added salt, one would naively expect a greater amount of surfactant to be required to induce phase separation, given the large values of $\lambda$ and the observation that increasing concentration increases the attractive contribution against the electrostatic stabilisation. Such expectations are fulfilled for the 175 and 105nm colloids. For the 70nm particles, however, we see that for with $\phi = 0.01$ (the colloid volume fraction at which the salt results were obtained) phase separation occurs around 0.009 g cm$^{-3}$ of C$_{16}$E$_6$, whilst in the case of salt the gas–liquid boundary is $\gtrsim 0.01$ g cm$^{-3}$. Indeed, even if the phase separation occurred at the same concentration of surfactant, it would be hard to explain how a system expected to be more stable against phase separation (because of the unscreened electrostatic repulsion between colloids) requires the same concentration of depletant micelles to phase separate. In Chapter 8 we shall discuss a possible explanation for this observation in terms of the electrical polarisation induced in the micelle excluding it from the vicinity of the colloids. The latter effect is the central idea [90, 89] underlying the work in this thesis, developed in the following chapters (starting from Chapter 4).

### 3.2.2 Charged Colloids and Uncharged Polymers

Mixtures of charged colloids and uncharged, non–adsorbing polymers in an aqueous solvent, provide a simpler instance of the kind of the electrostatic scenario we are interested in. The polymer solution is dilute, and the control parameter of the “effective” attractions between colloidal particles is the concentration of
polymers.

Early investigations using latex particles mixed with hydroxyethylcellulose or dextran in electrolyte solutions, found behaviour qualitatively similar to that displayed by colloidal hard spheres, with shifts in the phase boundaries due to the electrostatic interactions (see Section 10.7 of [24] and references therein).

Surprisingly, not many other investigations of mixtures of charged colloids are available in the literature, to the best of our knowledge. Recently, however, interest in charge has been revived by the treatment of proteins as colloids [13] and doubtless the biological drive of most soft matter research will force colloid scientists to investigate aqueous colloid–polymer mixtures.

### 3.3 Concluding Comments

In this chapter we hope to have given the reader an interesting view of some recent experiments relevant to the theory developed in this thesis. Of the experiments discussed, the experiments with lamellar phases doped with nonadsorbing polymers are the most directly relevant to the framework we shall construct in the following chapters. The simple model to follow in Chapter 4 will in fact be extended to describe polymers between flat surfaces in Chapter 5. This configuration is easily mapped to an approximate description of polymer doped lamellar phases, as will be shown in Chapter 6, from which predictions regarding the phase behaviour of such phases can be made (Chapter 7). This results are realistic enough to be compared with the experiments described in this chapter; however, given the approximations made in our model of polymers between surfaces (Model II of Chapter 5), the predicted results are only expected to strictly apply to nonadsorbing polymers (i.e. the experiments of Section 3.1.1).
Chapter 4

Model I: Dielectric Spheres

We consider here, through a minimal model, the possibility that double layer interactions may be affected by the presence of neutral, low permittivity molecules.

The idea is that non-uniform fields, such as the screened ones of electrical double layers, polarise dielectric solutes and can bias their distribution in the vicinity of charged surfaces which may in turn affect surface-surface interactions.

The model physics and formalism will be detailed next. Then it will be shown how the resulting equations have been solved. From the solutions the interaction (net osmotic pressure) between the surfaces is easily found, as we will show. Results will then be presented showing typical solutions to the equations and how the osmotic interactions are affected by changing the model parameters. We will then comment on the insights gained from this study. These insights are relatively minor. However, since the framework we will construct in this chapter will be built on in later chapters to give more subtle and interesting results than those found here, we will present the analysis in some detail. The basic concepts and relations resulting from the analysis will be useful to alleviate the discussion presented in later chapters.
4.1 Model Physics and Basic Assumptions

We wish to describe fatty molecules in an electrolyte solution in the neighborhood of ionised macroion surfaces, a situation not uncommon to soft matter systems, as shown Chapter 3.

In Section 2.6.3 it was explained how soft matter systems can be successfully approximated as electrostatic systems, and, in particular, how fatty molecules in an aqueous environment are often treated as low permittivity dielectrics. Adopting this philosophy, in our model we consider surfaces bearing a continuous distribution of charge (any macroion surfaces) bathed by an ideal aqueous mixture of pointlike charges (the macroion counterions and the added salt) and dielectric spheres (fatty molecules) of permittivity $\varepsilon_2$ and radius $a_d$. The spheres, despite having finite size, are, for the sake of simplicity, assumed to behave ideally at walls (no depletion effects) and at high concentrations. From a dielectric perspective the ionic solution, with which the spheres mix, is treated as a continuum with the permittivity $\varepsilon_1$ of the solvent (we thus neglects any dielectric influence of the ions$^1$), usually water ($\varepsilon_1 = 80$), as in the Gouy–Chapman model of Section 2.2.1. Figure 4.1 shows this simple abstraction of a real system.

From a thermodynamical point of view the system is in contact with a reservoir with which it can exchange heat, ions and dielectric spheres (see Section 4.2).

Before formulating the model mathematically, let us consider our expectations and get a feel for the magnitude of the "dielectric effect" (and provide ourselves with some reassurance that it is worth going through the toil of formulating and solving a model of it!).

4.1.1 Expectations

It is well known that dielectric media are electrically polarised by electric fields. Depending on the sign of the dielectric contrast with the embedding medium, the

$^1$This is a reasonably good approximation for dilute salt solutions [91]
field energy is raised or lowered by the work of polarisation required to charge the interfaces between the dielectric and the surrounding medium with equal and opposite charges. In addition, if the field is nonuniform the separate charges will experience different field intensities, causing dielectrics to energetically prefer regions of high or low field magnitude depending, in the same way as above, on dielectric contrast. A classical example of the latter effect is when a plastic slab is drawn into a parallel plate capacitor (in air) by the nonuniform field on the capacitor's edge. Similarly the change of field energy is exemplified by the use of insulating materials to increase the charge which can be stored in a capacitor.

When a solution of dielectric spheres (solutes) is placed in the neighborhood of a double layer we thus expect two effects. On one hand, the spheres, polarised by the electric field, will distribute themselves about the surface in a manner determined by the relative magnitudes of the randomising effect of thermal fluctuations and of the electrostatic energy they possess as a result of residing in the
CHAPTER 4. MODEL I: DIELECTRIC SPHERES

nonuniform field generated by the surface double layer. On the other hand, the net dipole fields induced at the interface between the spheres and the embedding electrolyte act to reduce the electric field (dielectric screening).

These effects, in general, are intrinsically coupled. It is useful, however, to obtain separate "limiting" estimates of the magnitude of each effect for realistic experimental conditions.

Effect of Field on Dielectric Spheres

What is the energy cost of keeping a low permittivity sphere close to a double layer?

A field $\mathbf{E}$ induces a dipole $\mathbf{p} = \alpha \mathbf{E}$ in the sphere, where $\alpha \simeq -K\varepsilon_1 a_d^3$ is the polarisability of the sphere of radius $a_d$ and polarisation (or Clausius–Mossotti) factor $K = (\varepsilon_1 - \varepsilon_2)/(2\varepsilon_1 + \varepsilon_2)$. From basic electrostatics, the force on a dipole in a nonuniform field is $\mathbf{F} = (\mathbf{p} \cdot \nabla)\mathbf{E}$. Consider a flat double layer. The energy of the dipole at location $x$ in front of the surface is found by integrating such force from infinity to $x$: $U_d(x) = -\int_{-\infty}^{x} \alpha E(dE/dx)dx = -(\alpha/2)E(x)^2$, where we have set $U_d(\infty) = 0$ and used $p = \alpha E(x)$. Substituting for $\alpha$, we can thus write the dielectric energy of a sphere, in units of $T$:

$$U_d/T \simeq K\varepsilon_1 E^2(x)a_d^3/T$$

(4.1)

Because $K > 0$ (the permittivity of the solvent, $\varepsilon_1$, is greater than that of the sphere $\varepsilon_2$), we see that the energy is smaller, as we move down the field gradient away from the surface.

We can estimate $E(x)$ at $x$ crudely from the solution of the 1D Debye–Hückel equation for an isolated double layer: $E(x) = E_s e^{-x/\lambda}$. Here $E_s$ is the surface field: $E_s = \sigma/\varepsilon_1$, $\sigma =$ surface charge, $\lambda$ is the Debye length. This neglects the influence of the sphere's "reaction field" on the surface field and assumes the
4.1. MODEL PHYSICS AND BASIC ASSUMPTIONS

Sphere is a point dipole at \( x \) (the field is uniform over the sphere). Equation (4.1) then becomes:

\[
\frac{U_d}{T} \approx K \left( \frac{\sigma^2}{\epsilon_1} \right) e^{-2x/\lambda a_d^3}/T
\]

Considering a sphere of radius \( a_d = 5 \text{Å} \), one Debye length away from a surface of charge \( \sigma = 0.01 \text{Cm}^{-2} \) (one charged group per \( 10^{11} \text{m}^2 \)), in a typical water–oil mixture with \( K \approx 1/2 \) (\( \epsilon_{\text{H}_2\text{O}} \approx 80 \), \( \epsilon_{\text{oil}} \approx 2 \)), at room temperature (\( 25\degree C \)), we find:

\[
U_d \sim 10^{-4} T \text{ per particle}
\]

so we need \( \sim 10^4 \) particles of this size joined together\(^{ii}\) (so as to have one translational mode), for the effect to be important (e.g. a long chain polymer with \( 5 \text{Å} \) radius monomers). Equivalently we would need a sphere with \( \approx 20 \) times the radius for the same surface charge or \( 100 \) times the surface charge for the same radius.

Effect of Dielectric Spheres on the Field

Here we estimate the global energetic overhead generated by the induced dipoles of a collection of spheres uniformly spread in front of a double layer, i.e. we assume thermal agitation is so violent that the field can’t move the spheres. It is also assumed that the dipoles do not modify the field, which is the same field \( \mathbf{E}_0 \) that would be produced by a “sphere–less” double layer. We recall the electrostatic energy of a dielectric medium is given by Equation (2.52):

\[
U_{el} = \int_{\mathcal{V}_1} \frac{1}{2} \mathbf{D}_0 \cdot \mathbf{E}_0 d\mathbf{r}
\]  \( (4.3) \)

\(^{ii}\)Neglecting variations of the field over the size of the conglomerate
where $V'$ is the volume of the region of interest. The electrical displacement of the
dielectric medium (electrolyte+spheres) is $D_0 \equiv \epsilon_1 E_0 + P$, where the polarisation
vector $P$ of a collection of spheres, of volume of $v_d$ and number density $n_d$, is
defined as $P \equiv n_d p$. Since, as for the previous estimate, the sphere's dipole
moment is $p = \alpha E_0$, and $\alpha = -3K \epsilon_1 v_d$ is its polarisability, Equation (4.3)
becomes:

$$U_{el} = (1 - 3K n_d v_d) \int_{V'} \frac{1}{2} \epsilon_1 E_0^2 \, dr$$

Letting $U_{el}^0 = \int_{V'} (1/2) \epsilon_1 E_0^2 \, dr$ define the sphere–less energy, and recalling the
volume fraction of spheres is $\phi_d = n_d v_d$, (4.4) can be rewritten as:

$$\frac{U_{el}}{U_{el}^0} = (1 - 3K \phi_d) < 1$$

For example, the electrostatic energy of a mixture containing $\phi_d = 0.1$ spheres,
will be about 90% of that of a pure electrolyte (where we have used $K \simeq 1/2$, as
in the previous estimate).

### 4.1.2 The Smoothing Approximation

The entropic contributions to the free energy of the minimal model system consist
simply of mixing terms, since we are considering an ideal solution. To model the
electrostatic contribution of the dielectric spheres to the free energy, we shall
adopt a mixing approach (see Section 2.4). The bulk electrostatic influence of
the dielectric spheres will thus be represented by an effective permittivity of
the mixture depending on the local sphere concentration $\phi_d$: $\epsilon_a = \epsilon_a(\phi_d)$. This
approximation is shown in figure 4.2.

Recall also from Section 2.4.1 that the approach involves averaging over regions
(of radius $R$) large with respect to the distance between inclusions ($\sim n^{-1/3}$)
and is thus a good approximation if $R \gg n^{-1/3}$ (Equation (2.40)). If the field
imposed on the dielectric is further changing on a characteristic scale (in our case the Debye length, $\lambda$), we also require $\lambda \gg R$, so that the field which is being averaged does not change in magnitude over the averaging volume. Thus, the smoothing approximation is strictly valid only if $\lambda \gg R \gg n^{-1/3}$ \textsuperscript{iii}. For the moderately concentrated mixtures we are interested in $\phi_d \gtrsim 0.1$, in which case $n^{-1/3} \sim a$, and the smoothing approximation is reasonable only if:

$$\lambda \gg a$$

(4.6)

### 4.1.3 An Expression for $\epsilon_e$

For the sake of simplicity, in Model I we will use the low concentration formula (2.44), for the effective permittivity of a mixture:

$$\epsilon_e(\phi_d) = \epsilon_1 (1 - 3K\phi_d)$$

where

\textsuperscript{iii}This approximation is also made when calculating the optical properties of composite materials [52]. In this case, the scale over which the electric field changes is the wavelength of the light incident on the dielectric.
Figure 4.3: Plot of the Maxwell—Garnett relation against its linear and low \( \phi_d \) limits. Only at very large \( \phi_d \) does the low \( \phi_d \) approximation start to be qualitatively wrong.

\[
K = \frac{\epsilon_1 - \epsilon_2}{2\epsilon_1 + \epsilon_2}
\]

is the Clausius-Mossotti factor.

Recall Equation (2.44) can be derived as the low concentration limit of the Maxwell—Garnett equation (Equation (2.42)). An alternative relation is sometimes used which covers the whole range of \( \phi_d \) (see the contribution by Khokhlov et al. in [39]) where the average dielectric constant is simply the sum of the component permittivities weighted by the volume fraction of each component:

\[
\epsilon_e(\phi_d) = \epsilon_0[\epsilon_2\phi + \epsilon_1(1 - \phi)].
\]

A plot of \( \epsilon_e(\phi_d) \) is shown for the three relations discussed is shown in Fig. 4.3.

### 4.2 Statistical Mechanical Formulation

Thermodynamically we shall operate in a grand canonical ensemble. The thermodynamic variables of the system are its volume, \( V \), temperature, \( T \), and chemical potentials \( \mu_i, i = +, - \), for the ions and \( \mu_d \) for the spheres. The thermodynamic
4.2. **STATISTICAL MECHANICAL FORMULATION**

potential minimised at equilibrium is the grand potential, which we shall denote by: \( \Omega(V, T, \mu_i, \mu_d) \).

The system volume is defined by the bounding charged surfaces, and the temperature and chemical potentials by the reservoir. Fig. 4.4 displays the thermodynamic setting of our model.

![Figure 4.4: The Thermodynamic Setting](image)

4.2.1 **The Free Energy Functional**

We expect the concentrations of species in our system to inhomogeneous: we know that ions will distribute according to the electric field, and expect the dielectric particles (and consequently the permittivity) to do the same. With these considerations in mind, it makes sense to write down the grand potential as a density functional:
\[ \Omega[n_i, n_d] = \int_V \left( \frac{1}{2} \epsilon_e n_d E^2 + T \sum_{i=+, -} n_i (\ln n_i - 1) + \right. \\
+ T n_d (\ln n_d - 1) - \sum_{i=+, -} \mu_i n_i - \mu_d n_d \right) \, dx \]  

Here, the first term is the electrostatic energy density of an electric field \( E \) in a medium of permittivity \( \epsilon_e \). The second term is the entropy of ions of number density \( n_i \), where \( i = + \) indicates positive ions and \( i = - \) negative ones (the entropy is that of translational mixing between ions and the solvent in an ideal solution). The third term is the entropic mixing of the dielectric spheres of number density \( n_d \) and the solvent. The last two terms account for the flow of particles from the reservoir.

The electric field must obey Maxwell’s equation relating electric displacement and free charge density:

\[ \nabla \cdot (\epsilon_e E) = \rho = \sum_{i=+, -} n_i q_i \]  

or equivalently in terms of the electrostatic potential \( V \) (where \( E = -\nabla V \)), Poisson’s equation:

\[ \nabla \cdot (\epsilon_e \nabla V) = -\rho = - \sum_{i=+, -} n_i q_i \]  

Formally Equation (4.9) provides a constraint relating the field and the ion number densities.

### 4.3 Variational Derivation of the Model’s Equations

The particle distributions which minimise the grand potential and obey Poisson’s equation correspond to the equilibrium state of the system.
4.3. VARIATIONAL DERIVATION OF THE MODEL’S EQUATIONS

Minimisation of functionals subject to differential constraints is possible [55], however it is more straightforward to use the variational methods introduced in Section 2.5.2.

4.3.1 Defining a Free Energy “Action”

We define the following free energy action (whose stationary value coincides with the functional (4.7)):

\[ A_\Omega[V, n_i, n_d] = \int_V a_\Omega(V, n_i, n_d) \, d\mathbf{r} = \int_V \left( -\frac{1}{2} \varepsilon_e(n_d)(\nabla V)^2 + \sum_{i=+, -, \ldots} n_i q_i V + T \sum_{i=+, -} n_i (\ln n_i - 1) + T n_d (\ln n_d - 1) - \sum_{i=+, -} \mu_i n_i - \mu_d n_d \right) \, d\mathbf{r} \]  (4.10)

Where \( a_\Omega \) is the position-dependent “action density” and all other symbols have been defined in (4.7).

4.3.2 “Equations of Motion”

Performing a variation with respect to the electrostatic potential \( \delta A_\Omega/\delta V = 0 \) or, equivalently, setting \( \frac{\partial a_\Omega}{\partial V} - \nabla \frac{\partial a_\Omega}{\partial V} = 0 \) we find the correct Maxwell equation:

\[ \nabla (\varepsilon_e(n_d) \nabla V) = - \sum_{i=+, -} n_i q_i \]

Notice how the spatially dependent dielectric constant is operated upon by the gradient, unlike the undergraduate textbook scenario of a spatially uniform dielectric constant.

Similarly a variation with respect to the ion number density \( \delta A_\Omega/\delta n_j = 0 \), i.e. \( \frac{\partial a_\Omega}{\partial n_j} - \nabla \frac{\partial a_\Omega}{\partial V n_j} = 0 \) yields the Boltzmann factor:
\[ n_i = n_i^r e^{-q_i V/T} \]

where \( n_i^r \equiv e^{-\mu_i/T} \) defines the chemical potential of ion \( i \), fixed by the reservoir.

Finally a variation with respect to the dielectric number density \( \delta A_\Omega/\delta n_d = 0 \), i.e. \( \frac{\delta A_\Omega}{\partial n_d} - \nabla \frac{\delta A_\Omega}{\partial \nabla n_d} = 0 \), gives:

\[ n_d = n_d^r e^{-\frac{1}{2} \frac{\partial \varepsilon_d}{\partial n_d} (\nabla V)^2/T} \]

where, as for the ions, \( n_d^r \equiv e^{-\mu_d/T} \) defines the chemical potential of the spheres and \( d\varepsilon_e(n_d)/dn_d = (d\varepsilon_e(\phi_d)/d\phi_d)(d\phi_d/dn_d) = (3/2)K\varepsilon_1 v_d \) (where \( v_d = (4/3)\pi a_d^3 \) is the dielectric volume). It is convenient to define the following constant: \( b = (3/2)K\varepsilon_1 v_d/T \).

We have thus derived the set of equations:

\[ \nabla (\varepsilon_e(n_d)\nabla V) = - \sum_{i=\pm} n_i q_i \]  
\[ (4.11) \]
\[ n_i = n_i^r e^{-q_i V/T} \]  
\[ (4.12) \]
\[ n_d = n_d^r e^{-b(\nabla V)^2} \]  
\[ (4.13) \]

These equations provide a complete description of the system to model. The Boltzmann particle distributions can be substituted in the Poisson-like equation to obtain a “Poisson–Boltzmann like” non-linear differential equation in \( V \):

\[ \nabla (\varepsilon_e(\nabla V)\nabla V) = - \sum_{i=\pm} n_i^r q_i e^{-q_i V/T} \]  
\[ (4.14) \]

where

\[ \varepsilon_e(\nabla V) = \varepsilon_1 (1 - 3K\phi_d^r e^{-b(\nabla V)^2}) \]  
\[ (4.15) \]
4.3. VARIATIONAL DERIVATION OF THE MODEL’S EQUATIONS

4.3.3 A Modified Debye–Hückel Equation (MDH)

To make things simple, we will use the Debye–Hückel (DH) approximation, which assumes the electrostatic energy of an ion is small with respect to its thermal energy. The linearisation is the same as for the ordinary DH equation (Equation (2.7)), since the mathematical form of the Boltzmann factor 4.12 is not affected by the inclusion of dielectric effects. Thus Equation (4.14) becomes:

$$\nabla (\varepsilon_c (\nabla V) \nabla V) = \kappa^2 V$$

(4.16)

where \( \kappa = \sqrt{\sum_{i=+,-} \frac{n_i q_i^2 / T}{\varepsilon_1}} \) is the inverse Debye length and \( \varepsilon_c \equiv \varepsilon / \varepsilon_1 \) is given by (4.15).

It is Equation (4.16) that we shall proceed to solve; it shall subsequently be referred to as the Modified Debye–Hückel Equation (MDH). From it all other physical quantities can be obtained, in particular, the net osmotic pressure between charged surfaces.

4.3.4 Osmotic Pressure

The difference in the osmotic pressure between the reservoir and our system determines the net “force” between the surfaces. The osmotic particles generating this pressure are the dispersed solutes (ions and dielectric molecules).

Here, once more borrowing mathematical methods of classical mechanics, we shall derive and expression for the net osmotic pressure of our system, and show how it is expressed in terms of the electrostatic potential and its gradient as determined by the solutions of Equation (4.16).

A Hamiltonian–like Conserved Quantity

The free energy action density \( a_\Omega \) in Equation (4.10) does not depend explicitly on the position at which it is evaluated. We can thus define a conserved quantity,
analogous to the Hamiltonian of classical mechanics:

$$\Pi := \sum_m p_m \nabla Q_m - a_\Omega = \text{const.} \quad (4.17)$$

where $a_\Omega$ is the free energy action density, and $Q_m$ and $p_m := \frac{\partial a_\Omega}{\partial \nabla Q_m}$ are the generalised coordinates and momenta of the problem. The right hand side of (4.17) is the conserved value of $\Pi$. In our case, recalling that $a_\Omega$ takes the form:

$$a_\Omega(V, n_i, n_d) = -\frac{1}{2} \epsilon_e(n_d)(\nabla V)^2 + \sum_{i=+, -} n_i q_i V +$$

$$+ T \sum_{i=+, -} n_i (\ln n_i - 1) - T n_d (\ln n_d - 1) - \sum_{i=+, -} \mu_i n_i - \mu_d n_d$$

the momenta are:

$$p_{n_i} = \frac{\partial a_\Omega}{\partial \nabla n_i} = 0; \quad p_{n_d} = \frac{\partial a_\Omega}{\partial \nabla n_d} = 0; \quad p_V = \frac{\partial a_\Omega}{\partial \nabla V} = -\epsilon(n_d) \nabla V; \quad (4.18)$$

so that we find by (4.17)

$$\Pi = p_V \nabla V - a_\Omega = -\frac{1}{2} \epsilon_e(n_d)(\nabla V)^2 - \sum_{i=+, -} n_i q_i V +$$

$$- T \sum_{i=+, -} n_i (\ln n_i - 1) - T n_d (\ln n_d - 1) + \sum_{i=+, -} \mu_i n_i + \mu_d n_d \quad (4.19)$$

We want to express $\Pi$ as a function of the electrostatic potential and its gradients. Substituting the expressions 4.12 and 4.13 for $n_i$ and $n_d$, and recalling the definition of the chemical potentials for for the reservoir species (Section 4.3.2), we have:
\[ \mathcal{II} = -\frac{1}{2} \epsilon_e (n_d) |\nabla V|^2 - \sum_{i=+, -} n_i^r e^{-q_iV/T} q_i V + T \sum_{i=+, -} n_i^r e^{-q_iV/T} (\ln n_i^r - q_i V/T - 1) + n_i^r e^{-q_iV/T} \ln n_i^r + T n_d^r e^{b(\nabla V)^2} (\ln n_d^r - b(\nabla V)^2 - 1) + T n_d^r e^{b(\nabla V)^2} \ln n_d^r = \text{const.} \] (4.20)

which can be simplified to:

\[ \mathcal{II} = -\frac{1}{2} \epsilon_e (n_d) |\nabla V|^2 + T n_d^r e^{-b(\nabla V)^2} b(\nabla V)^2 + T n_d^r e^{-b(\nabla V)^2} + T \sum_{i=+, -} n_i^r e^{-q_iV/T} = \text{const.} \] (4.21)

**Meaning of \( \mathcal{II} \)**

The physical meaning of \( \mathcal{II} \) is more easily seen if we rewrite Equation (4.21) as follows:

\[ \mathcal{II} = -\frac{1}{2} \epsilon_e |\mathbf{E}|^2 + n_d \frac{3}{2} K \epsilon_1 v_d |\mathbf{E}|^2 + \sum_{i=+, -} n_i T + n_d T = \text{const.} \]

where we have used \( \mathbf{E} = -\nabla V \), the Boltzmann factors for \( n_i \) and \( n_d \) are no longer explicitly expressed, \( b \) has been expanded to its definition \( (b \equiv (3/2)K \epsilon_1 v_d/T) \) and the dependency of the permittivity on \( n_d \) has been removed from the notation for clarity. Recalling, as in Section 4.1.1, that the polarisation vector \( \mathbf{P}_d \) of a collection of spheres of volume of \( v_d \) and number density \( n_d \), is defined as \( \mathbf{P}_d = n_d \mathbf{p} \) (where \( \mathbf{p} = \alpha \mathbf{E} \) is the dipole moment of each sphere and \( \alpha = -3K v_d \) is its polarisability), we have:

\[ \mathcal{II} = -\frac{1}{2} \epsilon_e |\mathbf{E}|^2 - \frac{1}{2} \mathbf{P}_d \cdot \mathbf{E} + \sum_{i=+, -} n_i T + n_d T = \text{const.} \] (4.22)
Let us, for a moment, ignore the dielectrics so that \( n_d = 0 \) and \( \epsilon_e = \epsilon_1 \). In this limit \( \Pi = -(1/2)\epsilon_1|E|^2 + \sum \eta_i T \), which makes it clear that \( \Pi \) represents the magnitude of the total stress normal to a surface in an electrolyte subject to a field \( E \). The latter has an osmotic contribution, which is the ideal solution pressure of the ions, and an electrostatic contribution, stemming from the pressure of the electric field on the surface (the Maxwell stress). In hydrostatic equilibrium, such contributions need to add up to a constant so that the force on the surface in a electrolyte is zero. The condition of equilibrium is thus equivalent to the conservation condition derived from the “Hamiltonian” formulation presented in this chapter.

This line of reasoning is extended to the case of added dielectrics: the second and fourth terms in (4.22) represent the electrostatic and osmotic contributions of the spheres to the normal stress of the electrolyte mixture. From now on we shall call \( \Pi \) an osmotic pressure, though this denomination is only strictly applicable if the electrostatic contribution vanishes.

**Net Osmotic Pressure in the Debye–Hückel Approximation**

In Section 4.3.3, we used the Debye–Hückel linearisation to simplify the form of the central equation of our model. Here, for consistency, we will do the same for the osmotic pressure. In this case however, the Boltzmann factor (4.12) needs to be expanded to second order (in the mean field the first order contributions to energy or pressure vanish because of electroneutrality):

\[
n_i = n_i^r \left( 1 - q_i V/T + \frac{1}{2} (q_i V/T)^2 + \mathcal{O} \left[ (q_i V/T)^3 \right] \right)
\]

Equation (4.21) thus becomes:
4.3. VARIATIONAL DERIVATION OF THE MODEL'S EQUATIONS

\[ \Pi = -\frac{1}{2} \varepsilon (\phi_d)(\nabla V)^2 + \frac{1}{2} \varepsilon_1 \kappa^2 V^2 + \]
\[ + T n_d^r e^{-b(\nabla V)^2} + T n_d^r e^{-b(\nabla V)^2} + T \sum_{i=+,-} n_i^r \]  \hspace{1cm} (4.23)

where \( \kappa \) is the inverse Debye length.

It is further useful to subtract the pressure of the reservoir from (4.23), so as to obtain an expression for the net force between surfaces. The reservoir pressure, \( \Pi^r \), consists simply of the osmotic contributions (and can be found from (4.23) by setting the electrostatic contributions to zero):

\[ \Pi^r = T n_d^r + T \sum_{i=+,-} n_i^r \]

and the net pressure is thus:

\[ \Pi_{net} = \Pi - \Pi^r \]
\[ = -\frac{1}{2} \varepsilon (\phi_d)(\nabla V)^2 + \frac{1}{2} \varepsilon_1 \kappa^2 V^2 + \]
\[ + T n_d^r \left( e^{-b(\nabla V)^2} + (1 + b(\nabla V)^2) - 1 \right) \]  \hspace{1cm} (4.24)

**Exploiting the "Conservation" of \( \Pi \)**

Since the value \( \Pi \), for a given system volume (boundary conditions), does not depend on the position between surfaces, it is often conveniently evaluated where some of the contributing terms vanish. For example, in the case of opposing flat surfaces, the electric field vanishes at the midplane by symmetry. This makes Equation (4.24) particularly simple, as we will see in Section 4.4.1.
4.4 Solving the Model

At this point it is possible to obtain results for the net osmotic pressure between plates as a function of the separation between them for different “experimental conditions”.

The plan is to solve the MDH equation (4.16) for the case of flat parallel charged surfaces of infinite extent for suitable boundary conditions and a given separation. By substituting the solutions evaluated at a convenient (in the sense explained in the preceding section) position between the plates, it is then possible to evaluate the osmotic pressure at that separation. The procedure can then be repeated for different surface spacings and the desired pressure–separation profiles obtained.

Before discussing the solutions, we will show how to adapt the general equations derived to the particular problem at hand. Further, the variables will be made dimensionless for the purposes of numerical solution and to highlight the dimensionless parameters characterising the scales of the problem.

4.4.1 Setting Up for Solution

1D MDH and Dimensionless Variables

Parallel surfaces have a high degree of symmetry, since we assume they are infinite in the directions parallel to their surface. The natural coordinate system of the problem is a one dimensional cartesian set, whose position variable we shall denote by \( x \) and origin on the “leftmost” surface (shown in Fig. 4.5 for the dimensionless variables).

With these conventions the one dimensional form of (4.16) reads:

\[
\frac{d}{dx} \left( \tilde{\varepsilon}(V') \frac{dV}{dx} \right) = \kappa^2 V
\]  

(4.25)
where $\tilde{\epsilon}_e(V') = 1 - 3K\phi_d e^{-b(V')^2}$ and from now on we shall use primed notation as an alternative to differential notation to indicate derivatives w.r.t. $x$: $f'(x) \equiv df(x)/dx$ or $f''(x) \equiv d^2f(x)/dx^2$.

Next, we can rescale the potential and the $x$ coordinate to the characteristic potential and length scales of the problem: the surface potential, $V_s$ and the Debye screening length, $\lambda$. Let us define:

$$W \equiv \frac{V}{V_s}; \quad X \equiv \frac{x}{\lambda};$$

Thus (4.25) becomes:

$$\frac{d}{dX} \left( \tilde{\epsilon}_e(W') \frac{dW}{dX} \right) = W$$

(4.26)

where now $\tilde{\epsilon}_e(W') = 1 - 3A e^{-B(W')^2}$ and we have defined $A \equiv 3K\phi_d$ and $B \equiv bV_s/\lambda = 3K\epsilon_1(V_s/\lambda)^2\nu_d/2$. Then:

$$\frac{d}{dX} \left( (1 - A e^{-B(W')^2}) \frac{dW}{dX} \right) = W$$

(4.27)

This is a non-linear second order differential equation. To see this more clearly, let us explicitly carry out the differentiation on left hand side:

$$W'' - Ae^{-B(W')^2}W'' + 2ABe^{-B(W')^2}(W')^2W'' - W = 0$$

(4.28)

We see that the derivative of the unknown potential $W(X)$ appears in exponential and quadratic form. For our purposes, a horrible equation like this is easily solved numerically.

**Boundary Conditions**

We saw in Section 2.2.2 how approaching charged surfaces can be approximated as having either fixed surface potential or fixed surface charge upon approach. For
the purposes of this chapter either condition would have been satisfactory, but for our model, the condition of surface charge is complicated by the assumption of ideality of the dielectric spheres. To see this recall that the field at the surface, for positively charged surfaces with charge density $\sigma$, is given by $E_s = \sigma / \epsilon$ (Equation (2.13)) and in our case $\epsilon = \epsilon_e(\phi_d|_s)$, where $\phi_d|_s = \phi_d^e e^{-bE^2}$. Thus the surface charge density $\sigma$ does not univocally determine the surface electric field, whose knowledge depends on the local permittivity and vice versa. A selfconsistent solution subject to this "functional" boundary condition would be required.

The constant surface potential boundary condition is not affected by these problems, and will thus be adopted. We consider two situations: that of equal surface potentials (implying that the electric field vanishes at the midplane) and that of unequal surface potentials. These boundary conditions read:

\begin{align*}
V|_{x=0} &= V_{s1} \quad \text{ (unequal potentials)} \\
V|_{x=d} &= V_{s2}
\end{align*}

(4.29) (4.30)
4.4. SOLVING THE MODEL

\[ V|_{x=0} = V_s = V|_{x=d} \quad \text{(equal potentials)} \quad (4.31) \]
\[ \Leftrightarrow V'_{x=d/2} = 0 \]

where \( V_{s1,2} \) is the value of the potentials at each surface and \( d \) is the separation between surfaces. In reduced variables, the above become:

\[ W|_{X=0} = W_{s1} \quad \text{(unequal potentials)} \quad (4.32) \]
\[ W|_{X=H} = W_{s2} \quad (4.33) \]

\[ W|_{X=0} = W_s = W|_{X=H} \quad \text{(equal potentials)} \quad (4.34) \]
\[ \Leftrightarrow W'_{X=H/2} = 0 \]

and the surface geometry is shown in Fig. 4.5.

We are thus ready to solve Equation (4.28) for \( W(X) \), subject to (4.32)–(4.33) or (4.34). In particular, evaluating the potential at the midplane, we can calculate the osmotic pressure between the plates.

**Osmotic Pressure**

Equation (4.24) can also be recast in a 1D dimensionless form in terms of the dimensionless potential \( W \):

\[ \Pi_{net} = \pi_{ions} \left[ W_{H/2}^2 - (W')_{H/2}^2 \right] + \pi_{diele} \left[ e^{-B(W')}_{H/2} \left( 1 + B(W')_{H/2}^2 \right) - 1 \right] \]

where we have defined the constants: \( \pi_{ions} \equiv (1/2)\epsilon_1(V_s/\lambda)^2 \) and \( \pi_{diele} \equiv n_d' T = (\phi_d'/v_d)T \), with dimensions of pressure.
\( \Pi_{\text{net}} \) can be conveniently evaluated at any position between the plates, since it is a conserved quantity (Section 4.3.4). For the symmetric boundary conditions, the field vanishes at the midplane at \( X = H/2 \) ((4.34)). For asymmetric boundary conditions, it will vanish elsewhere, depending on the relative magnitude of the surface potential, we will thus keep the full expression for the asymmetric case, also evaluated at the midplane.

For these boundary conditions the expression of the pressure as a function of the plate separation is thus:

\[
P_{\text{Asym}} = \left[ W_{H/2}^2 - (W')_{H/2}^2 \right] + \pi_{\text{rel}} \left[ e^{-B(W')_{H/2}^2} \left( 1 + B(W')^2_{H/2} \right) - 1 \right] \tag{4.35}
\]

\[
P_{\text{Sym}} = W_{H/2}^2 \tag{4.36}
\]

where we have defined the dimensionless pressures \( P \equiv \Pi_{\text{net}} / \pi_{\text{ions}} \) and \( \pi_{\text{rel}} \equiv \pi_{\text{die}} / \pi_{\text{ions}} \) for symmetric and asymmetric boundary conditions, respectively. We note that since \( W_{H/2}^2 \) is always positive for finite separations between the surfaces, the net pressure in the symmetric case will always be repulsive.

We shall shortly look at plots of (4.35) and (4.36) (Section 4.5). Before that, however, it is useful to consider two extreme limits in which equation (4.27) reduces to an analytically solvable Debye–Hückel equation.

### 4.4.2 Limiting Solutions and Orders of Magnitude

Equation (4.27) contains two constants \( A \) and \( B \); we can set these independently to 0, to find analytic limit solutions of the horrible (4.28). But what do such limits mean physically?

**Meaning of \( A \) and \( B \)**

Recall the definitions of \( A \) and \( B \):
4.4. SOLVING THE MODEL

\[ A \equiv 3K\phi_d^r \]
\[ B \equiv 3K\epsilon_1(1/2)(E_s^\infty)^2v_d/T \]

Where we have defined \( E_s(H \to \infty) \equiv E_s^\infty = V_s/\lambda \), the surface field in the limit of an isolated surface.

The meaning of \( A \) and \( B \) has thus already been discussed in Section 4.1.1: \( B \) sets the energy scale of a dielectric sphere in thermal units, \( A \) the maximum amount by which electrostatic energy is reduced by the presence of a uniform concentration of spherical dipoles. Equation (4.27) expresses such meaning in the language of our model: \( B \) is the dimensionless constant that determines the magnitude of the Boltzmann factor for the distribution of spheres; \( A \) sets the overall reduction of the effective dielectric constant of the mixture.

\[ A = 0 \text{ or } B \to \infty \text{ limit: No Dielectric} \]

\( A \) can also be thought of as a “coupling constant”. \( A \) can vanish either because there is no dielectric contrast between the spheres and the embedding solution (\( K = 0 \)) or, trivially, because there are no spheres at all (\( \phi_d^r = 0 \)). In this limit, the effect of the dielectric solutes is removed and the the surfaces interact across a “standard” electrolyte.

For \( A \neq 0 \) an effect equivalent to setting \( A = 0 \) can be obtained by making \( B \) very large: the energetic cost of keeping spheres in the field is a high price to pay. This can be arranged by lowering temperature, increasing the dielectric volume, \( v_d \) or increasing the field strength, \( V_s/\lambda \). Strictly, the latter two conditions in our model are limited by the applicability of the smoothing and Debye–Hückel approximations (described in Sections 4.1.2 and 4.3.3), respectively. [We shall nevertheless increase these parameters when studying the results of Section 4.5 for the reasons explained in Section 4.5.2].
The effect of dielectrics is removed if $B$ is very large; the spheres flee to where there is no field and where, because they are sizeless, they have no effect\textsuperscript{iv}: the midplane between the surfaces.

If $A = 0$ (4.27) is simply:

$$\frac{d^2W}{dX^2} = W$$

(4.37)

Which is a rescaled version of the Debye–Hückel equation. Its solutions for parallel plates at constant potential are:

$$W_{\text{Asym}}^A(X) = \left( \frac{W_{s1} + W_{s2}}{2} \right) \frac{\cosh(X - H/2)}{\cosh(H/2)} + \left( \frac{W_{s1} - W_{s2}}{2} \right) \frac{\sinh(X - H/2)}{\sinh(H/2)}$$

(4.38)

$$W_{\text{Sym}}^A(X) = \frac{\cosh(X - H/2)}{\cosh(H/2)}$$

(4.39)

In our results the near surface potentials in the asymmetric case will always be greater than the far values so that $W_{s1} = 1$ and $W_{s2} = f$, where $f$ is a number between 0 and 1. Note how the solutions reflect the symmetry of the boundary conditions: the symmetric solution is the even function $\cosh$; the asymmetric solution is a linear combination of symmetric and antisymmetric contributions, weighted by the averaged sums and differences of the surface potentials.

**Osmotic Pressure**

It is then easy to find a limiting expression for the osmotic pressure by substituting the above solutions into equations (4.35) and (4.36):

\textsuperscript{iv}In the next chapter we will amend this unrealistic situation by including excluded volume and correlation contributions.
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\[ P_{A\rightarrow 0}^{A-0}(H) = \left[ \frac{(W_{s1} + W_{s2})^2}{2} \frac{1}{\cosh^2(H/2)} + \right. \]

\[ \left. - \left( \frac{W_{s1} - W_{s2}}{2} \right)^2 \frac{1}{\sinh^2(H/2)} \right] \]

\[ P_{S\rightarrow 0}^{A-0}(H) = \frac{1}{\cosh^2(H/2)} \]  

which is simply the net pressure due to ions and/or electrical stress at the mid-plane, since setting \( A = 0 \) removes the dielectric contribution (\( \phi_d = 0 \) means \( n_d^r = 0 \) for fixed \( a_d \)).

\( B \rightarrow 0 \) limit: Uniform Dielectric Mixtures

\( B \) can also be thought of as a measure of the spread of the spheres. For \( A \neq 0 \), we can make \( B \) very small by making the spheres tiny, \( v_d \rightarrow 0 \) (at fixed \( \phi_d^r \)) or the temperature very high \( T \rightarrow \infty \). In this limit the spheres are uniformly spread between the plates: they stay put, since there is no energetic cost for them to reside in a non-uniform field. In this scenario, the mixture is a solution with a uniform dielectric constant, which is reduced from the no-sphere value by a factor of \( 1 - A \).

If \( B = 0 \) (4.27) becomes:

\[ \frac{d^2W}{dX^2} = \frac{W}{C^2} \]

Again this is just a Debye–Hückel type equation. The solutions are the same as in the preceding section, except that the lengthscales are reduced by a factor of \( C \equiv 1/\sqrt{1 - A} \):

\(^{\text{vWe don't want to remove the surface field, since we want a situation that we can compare to an ordinary double layer.}}\)
\[ W_{\text{asy}m}^{B-0}(X) = \left( \frac{W_{s1} + W_{s2}}{2} \right) \frac{\cosh(C(X - H/2))}{\cosh(C(H/2))} + \left( \frac{W_{s1} - W_{s2}}{2} \right) \frac{\sinh(C(X - H/2))}{\sinh(C(H/2))} \] (4.43)

\[ W_{\text{sym}}^{B-0}(X) = \frac{\cosh(C(X - H/2))}{\cosh(C(H/2))} \] (4.44)

The above solutions describe a medium whose the Debye length of the electrolyte is reduced by a factor of \( C = \sqrt{1 - 3K\phi_d^2} \) (< 1):

\[ \lambda_u = \lambda \sqrt{1 - 3K\phi_d^2} \] (4.45)

This, in turn, is the simple consequence of having a reduced the permittivity by a factor \( C^2 : \epsilon = \epsilon_1(1 - 3K\phi_d^2) \) [recall \( \lambda(\epsilon) \equiv \sqrt{\epsilon T/(\sum_{i=-,+} n_i q_i^2)} \)].

**Osmotic Pressure**

As for the \( A = 0 \) limit, with the above solutions we can find a limiting expression for the osmotic pressure substituting the above solutions into equations (4.35) and (4.36):

\[ P_{\text{asy}m}^{A-0}(H) = \left[ \left( \frac{W_{s1} + W_{s2}}{2} \right)^2 \frac{1}{\cosh^2(C(H/2))} \right] + \] (4.46)

\[ - \left( \frac{W_{s1} - W_{s2}}{2} \right)^2 \frac{1}{\sinh^2(C(H/2))} \]

\[ P_{\text{sym}}^{A-0}(H) = \frac{1}{\cosh^2(C(H/2))} \] (4.47)

which is again the pressure due to ions and/or electrical stresses at the midplane, since setting \( B = 0 \) removes the dielectric contribution in (4.35).
4.5. RESULTS

4.5 Results

In this section we shall present the predictions of Model I for the net osmotic interaction between parallel charged surfaces.

After a survey of the graphs of main physical quantities which result from a solution of Equation (4.28) for a particular plate separation, we will study the effect of parameter variation on the osmotic pressure. For all cases, the results have been "bracketed" by the analytic limits of Section 4.4.2, which also furnish a key of interpretation of the results.

We have chosen experimentally reasonable values (Section 4.5.2) for the physical parameters in the numerical solution of the Equation (4.28) (from which the osmotic pressure is derived); however, the approximations of our model have been taken to or beyond their strict limits to explore the strength of the dependence of the parameter under investigation, as well as the effect of electrostatic coupling.

4.5.1 Numerics

Numerical solutions of the ordinary differential equation (4.28), subject to the boundary conditions (4.32), (4.33) for the asymmetric case and condition (4.34) for the symmetric case, were obtained using the standard Runge-Kutta fourth order ODE solver (see Chap. 16 of [92]).

The general ODE solver was set within a code, written to solve of our particular problem: a single run would produce the numerical data used to graph the solutions of (4.28) for a typical $H$ and the osmotic pressure profiles (presented from Section 4.5.3 onwards). The details of the code and the uncertainties associated with the results are described in Appendix A.
4.5.2 Parameters Used

Table 4.1 defines a set of “basis” parameters. When explaining trends on varying some particular parameter, we keep these fixed, with exception of the parameter under study. For a few cases, different “basis parameters”, have been used, in which case their values will be appropriately quoted in the text.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elementary charge</td>
<td>$e = 1.6 \times 10^{-19}$ C</td>
</tr>
<tr>
<td>Permittivity of vacuum</td>
<td>$\varepsilon_0 = 8.85 \times 10^{-12}$ F m$^{-1}$</td>
</tr>
<tr>
<td>Boltzmann’s constant</td>
<td>$k_b = 1.38 \times 10^{-23}$ J K$^{-1}$</td>
</tr>
<tr>
<td>Temperature</td>
<td>$T = 298$ K</td>
</tr>
<tr>
<td>Surface Potential</td>
<td>$V_s = 100$ mV</td>
</tr>
<tr>
<td>Debye length</td>
<td>$\lambda = 800$ Å (80 nm)</td>
</tr>
<tr>
<td>Permittivity of ionic solution</td>
<td>$\varepsilon_1 = 80$</td>
</tr>
<tr>
<td>Permittivity of spheres</td>
<td>$\varepsilon_2 = 2$</td>
</tr>
<tr>
<td>Dielectric Sphere Radius</td>
<td>$a_d = 80$ Å</td>
</tr>
<tr>
<td>Reservoir Sphere Volume Fraction</td>
<td>$\phi_d^r = 0.4$</td>
</tr>
</tbody>
</table>

Table 4.1: Parameters used to solve Model I

The first three values from the top of Table 4.1 are fundamental constants, which need no comment. When an aqueous electrolyte is the host solvent, $\varepsilon_1 = 80$ and $T = 298K$ are typical values for the permittivity and temperature (recall we ignore the effect of salt on $\varepsilon_1$).

$V_s$ is the constant potential at the charged surfaces. A value of 100 mV is quite typical for moderately charged complex fluids (for an isolated surface in a mM salt solution this value would correspond to a surface charge of $\approx 1e$ per 100 nm$^2$).

When the effect of $V_s$ was studied, its value was in the range 10 — 200 mV; when studying other parameters $V_s$ was sometimes increased to 300 mV for the purpose of enhancing the “dielectric effects” we have been discussing in this chapter. Strictly, using high values of $V_s$ (> 25 mV) undermines the condition of validity.
of the Debye–Hückel linearisation, (2.14). However, as discussed in Section 2.2.4, the Debye–Hückel approach yields results which are qualitatively correct with regards to the electrostatic fields, even quite far outside its regime of validity, when one is interested only in “field effects” and not in the ion distributions. A further point to notice is that since both the ions and the dielectric spheres reside in a thermal bath, increasing $V_s$ could be thought of as equivalent to reducing temperature\textsuperscript{vi}.

The Debye length $\lambda$ is defined in the absence of the dielectric: for a system in contact with of pure electrolyte, $\lambda$ is found from the concentration $c^e$ of electrolyte (Section 2.2.1). Using Equation (2.10) we have evaluated the Debye lengths corresponding to experimentally used concentrations of monovalent salts: $\lambda = 50 - 800\, \text{Å} \ (c^e=10^{-5} - 0.004M)$; the largest value of $\lambda$ was calculated from the smallest salt concentration to be found in experimental literature on charged systems [93].

The dielectric constant $\varepsilon_2$ describes any substance whose permittivity is measurably different and, in our case, smaller than that of the solvent: in the present study (and in the following chapters of the thesis) $\varepsilon_2$ is varied in the range $2 - 70$. $\varepsilon_2 \simeq 2$ for any water soluble substance with a substantial proportion of non–polar groups (e.g. alkanes). This assumption is often made when treating the oily cores of micelles or membranes. Realistically, however, if such “oily” compounds are to reside in water, they have to possess a hydrophilic group (e.g.: artificial membranes are actually filled with surfactants and alcohols whose oily tails form the inner bilayer, see Chapter 3); in this thesis we ignore the electrical contribution of the hydrophilic groups\textsuperscript{vii}. The intermediate values of $\varepsilon_2 \simeq 10 - 30$ used when studying the effect changing $\varepsilon_2$ in Section 4.5.4, can be considered to be the permittivities of proteins [94] or alcohols (see Table 3.2 of [18]). For higher still

\textsuperscript{vi}Though clearly severe increases would imply cooling the system to the realm of low temperatures where entirely different physics is at play. In fact even moderate temperature reductions might be problematic, since phenomena such as ion condensation effects might arise.

\textsuperscript{vii}A more sophisticated model with layered dielectric inclusions could conceivably be built, see sect. 4.3 of [53].
values \((\varepsilon_2 = 50 - 70)\) we could find no real correspondent at room temperature.

Parameter \(a_d\) represents the dielectric sphere radius determining the polarisable volume \(v_d\). The range of values used, \(a_d = 5 - 80\ \text{Å}\) (with \(a_d\) always at least 1/10th of \(\lambda\) to preserve the validity of the smoothing approximation), were inspired by the size of real low permittivity solutes: from isolated long chain hydrocarbons, such as alcohols or non-ionic surfactants (length \(\sim 10\text{Å}\)) and their micelles (diameter \(\sim 20 - 40\text{Å}\)) \([95, 89]\) to microemulsion droplets (diameter \(\sim 160\text{Å}\)) \([96]\).

### 4.5.3 Physical Predictions of the MDH Equation at given \(H\)

Presented in Fig. 4.6 is a snapshot of four main physical quantities obtained from the solution of the MDH (4.26), for a typical inter—surface spacing of \(H = 4\). The potential \(W(X)\) (Fig. 4.6a) and the electric field, \(F(X) = -W'(X)\) (Fig. 4.6b), are compared with the analytic solutions (4.39) and (4.44) in the limits \(A = 0\) and \(B = 0\), respectively. On the plot (Fig. 4.6d) for the volume fraction of spheres \(\phi_d(X)\), a solid line is drawn at the reservoir value \(\phi_d^* = 0.35\). The permittivity of the solvent at \(\varepsilon_1 = 80\) is also drawn as a solid line on the Fig. 4.6e, which displays the variation of the effective permittivity \(\varepsilon_e\).

We see that for this separation between the surfaces and for the parameters chosen, the potential (Fig. 4.6a) has, as could be expected, a similar symmetric shape to a solution to a “standard” Debye—Hückel equation, exemplified by the two limit solutions. These bracket the MDH potential profile, which doesn’t, however, differ significantly from the “uniform dielectric mixture” solution \((B = 0\) limit). The electric field (Fig. 4.6b) is antisymmetric, also as expected. Close to the surface, its magnitude is greater than that of an ordinary electrolyte solution \((A = 0\) limit) and smaller that the “uniform dielectric mixture” limit close to the surface; this is not however the case in an extended region about the midplane (Fig. 4.6b2) for reasons which will soon be evident. Fig. 4.6c displays the positive and negative ionic profiles predicted in the Debye—Hückel approximation; the latter is violated, since \(V_s > 25\text{mV}\), which entails unphysical negative number
Figure 4.6: Variation with position $X$ of the dimensionless: (a) electrostatic potential $W$; (b) electric field $F$ (magnified in b2); (c) ion densities; (d) dielectric volume fraction; and (e) dielectric constant. The solutions are compared with the limits discussed in the text and have been found using the parameters of Table 4.1 and $H = 4$. 
densities of positive ions (salt) away from the midplanes. This is of no consequence for qualitative predictions, if we are not interested in describing the Donnan balance of salt. The results suggest that the number of "pressure determining" salt ions at the midplane is larger than the pure electrolyte case: the dielectric mixture possesses a greater ability to screen electrostatic interactions because polarisation induced charges can also participate in the screening process. This will, in turn, reduce the potential in which the ions move (as we saw in Fig. 4.6a).

Looking at the distribution of spheres (volume fraction) in Fig. 4.6d we notice that the field has caused a depletion of spheres from the surfaces, though a finite surface concentration is present there. We see that at the midplane, since the field is zero, the concentration of spheres is equal to that of the reservoir. The depletion of spheres from the surfaces reflects on the permittivity (Fig. 4.6d), which similarly doesn't reach the pure water value at the walls and becomes that of a "static" dielectric mixture at the midplane.

The distribution of spheres can help to understand the form of the electric field. We see that the surface field is larger than that of a pure electrolyte system, since the nonzero volume fraction of spheres reduces the value of the effective permittivity at the surface, but smaller that that of the uniformly distributed spheres, since the latter are not depleted from the surface and further reduce the permittivity.

To understand the form of the electric field in the region around the midplane (Fig. 4.6b2), it is sufficient to recall that dipoles induced by a nonuniform field can act as source of polarisation charge, which can cause the electric field to rise above the values of a uniform medium. This is a result of the fact that the displacement $\mathbf{D}$ is the natural field of the problem, not the electric field.

In Fig. 4.7, we have increased $V_s$ to 300 mV (with all the other parameters unchanged) and reduces the surface spacing to $H = 3.23$, and we have plotted the dimensionless displacement $D/\varepsilon_1$ as well as the field. We see when $D/\varepsilon_1$ is plotted the MDH result is properly bracketed between the two limits. All the
Figure 4.7: Variation with position $X$ of the dimensionless: (a) electrostatic potential $W$; (b) electric field $F$ (magnified in b2); (c) ion densities; (d) dielectric volume fraction; and (e) dielectric constant. The solutions are compared with the limits discussed in the text and have been found using the parameters of Table 4.1, except here $V_o = 300 \, \text{mV}$ and $H = 3.23$. 
other physical quantities are also shown for this high surface potential. We shall not comment on them in detail, but to notice that the depletion of spheres is more pronounced for this $V_s$, as one would expect given the higher energetic price paid by the spheres, making the inter-surface material more water-like. This reflects on the electrostatics which only differs from the pure electrolyte limit near the midplane, where the concentration of spheres must return to the reservoir value because there is no field. If a nonlocal field dependence were introduced, one could well imagine the possibility of an electrostatically driven depletion attraction between the surface (a topic which we will return to in Chapter 5).

4.5.4 Osmotic Pressure Profiles, Equal Surface Potentials

Surface and Solution Parameters

Effect of Surface Potential

Let us now change the surface potential and see how the net pressure is affected (Fig. 4.8).

The first thing to notice is that the pressure is always positive: the charged surfaces will repel when the spheres are present, just as for the pure electrolyte case ($A = 0$). This is a general feature of Model I, and is due to the fact that, for each value of $H$, the conserved pressure is identical to the ion pressure at the midplane, which is always greater than that in the reservoir for finite separations (as we saw in Section 4.4.1).

However, the repulsion is reduced with respect to a pure electrolyte: $P_{sym}$ is halved for $V_s = 10$ mV and $H \approx 2$. The reduction of the pressure, $\sim W_H^{2/3}$, is due to the “extra screening” contributed by the spheres, discussed in the previous section. For low $V_s$, the reduced repulsion is well approximated by the $B = 0$ limit of uniformly spread dipoles; in this limit the electric field generated by the surface is not of sufficient magnitude to make the surfaces inaccessible to thermal
diffusion of the spheres (the Boltzmann distribution is uniform). The average
dielectric constant of the interplate medium is that of a medium embedded with a
uniform distribution of induced dipoles, so that the osmotic repulsion is uniformly
reduced.

As the potential is increased the pressure profile "peels off" from the $B = 0$ limit
for intermediate values of the surface separation $H$. This is because the distri-
bution of spheres becomes more and more concentrated around the midplane, as
$V_s$ is raised (see Fig. 4.7d); this depletion from the surfaces makes the interplate
medium increasingly water like, and $\epsilon_e$ increases towards $\epsilon_1$. The pressure reflects
this change at intermediate separations, where the field is strong and nonuniform.
At large values of $H$, where the midplane electrostatic influence has decayed away,
the numerical results converge back onto the uniform dielectric mixture limit.
Effect of $\lambda$ (reservoir salt concentration)

Next we look at the effect of increasing the reservoir Debye length $\lambda$, by decreasing the reservoir salt concentration. Fig. 4.9 shows how a progressive increase of $\lambda$ moves the pressure profiles towards the lower analytic limit ($B = 0$). To make the variations with $\lambda$ more evident, the results have been obtained with the surface potential increased to $V_s = 300$ mV and the sphere radius used was changed to 40 Å. (How these increases relate to our approximations has been discussed earlier in Section 4.5.2 and in Section 4.5.3).

![Graph showing the effect of $\lambda$ variation on pressure](image)

Figure 4.9: Study of the effect of $\lambda$ variation on pressure. The numerical data has been obtained using the values of Table 4.1, except here $V_s = 300$ mV, $a_d = 40$ Å and $\phi_d = 0.4$ for the reasons discussed in the text.

For this set of parameters, the MDH pressures form a band which is “thin” at large and small separations, where it overlaps with the $B = 0$ limit pressure and “fat” at intermediate separations, displaying a profile bracketed by the analytic limits. The deviation from the $B = 0$ limit is less marked for the larger values of $\lambda$. We can explain this trend by noting that, for each separation $H$, the electric field progressively becomes more uniform as $\lambda$ is increased and thus the dielectric
spheres become increasingly happy close to the surface, making the medium less water like and more like a uniform dielectric mixture.

**4.5. RESULTS**

Dielectric Sphere Parameters

Effect of $a_d$

Fig. 4.10 displays the sensitivity of the pressure to changes in the sphere radius. For the same reasons as for the study of $\lambda$, we have here set $V_s = 300 \text{ mV}$ and $\lambda = 800 \text{ Å (80 nm)}$.

![Graph showing effect of $a_d$ on pressure](image)

Figure 4.10: Study of the effect of $a_d$ variation on pressure. The numerical data has been obtained using the values of Table 4.1, except here $V_s = 300 \text{ mV}$, $a_d = 40 \text{ Å}$ and $\phi_d = 0.4$ for the reasons discussed in the text.\(^1\)

Increasing the sphere radius shifts the profiles from the neighborhood of the limit of uniform dielectric mixture, $B = 0$, to the “pure electrolyte with spheres at the

\(^1\)The $a_d = 5$ set is cut off for reasons of numerical accuracy. Time did not allow to amend this result. However, since we have no reason to expect that an increase in accuracy will yield results different from the other results in this chapter, we can reasonably expect the pressure to carry on smoothly after $H=2$.\)
midplane" $A = 0$ scenario. This is because an increase in the polarisable volume of a sphere increases its energy in the field so that at intermediate separations the spheres deplete from the surfaces.

We notice that the pressure profiles are more sensitive to changes in $a_d$ than to changes in $\lambda$. This is easily understood if we consider that the dielectric energy scales like $a_d^3$ and like $\lambda^{-2}$.

**Effect of Dielectric Contrast**

In Fig. 4.11 we have changed the permittivity $\epsilon_2$ of the spheres to investigate the dependence of pressure on dielectric contrast between solutes and solvent (here the parameters used to obtain Fig. 4.11 have been restored to those of Table 4.1, except here $\phi^r = 0.35$). Note that changing $\epsilon_2$ affects the $B = 0$ limiting solution since the value of $A = 3K\phi_0^r$ (which, remember, is a measure of the maximum effect of dielectrics and determines the reduction of the Debye length in this limit, see Section 4.4.2) is also a function of dielectric contrast. Thus, for each of the numerical profiles, a different limiting curve is plotted.

As expected, as $\epsilon_2$ is increased from the value of oil to a value close to that of water the pressure profiles move toward the pure electrolyte limit. In fact an increase in $\epsilon_2$ is like making the spheres more and more ghostlike for the field, until when $\epsilon_2 = \epsilon_1$ they are no longer discernible (this can be used to check the numerics is well behaved, as reported in Section A.3 of Appendix A).

It is interesting to notice how for permittivity values above $\epsilon_2 \gtrsim 25$ the lower analytic solution is an increasingly accurate approximation to the coupled behaviour. This is obvious, considering that the departure from the lower limit depends on the magnitude of $B$, which depends in the same way on dielectric contrast (via the factor $K$). Also as the contrast disappears the upper and lower limit and the numerical solution all merge to describe the same "sphere-less" electrolyte, as one would expect.
4.5. RESULTS

Figure 4.11: Study of the effect of $\varepsilon_2$ variation on pressure. The numerical data has been obtained using the values of Table 4.1, except here $\phi^r = 0.35$.

Effect of Sphere Concentration

Finally, in Fig. 4.12 we look at the effect of changing the reservoir sphere concentration. The surface potential has now been restored to a more conservative 100 mV and all other parameters are also as in Table 4.1. The results were calculated for two different dielectric radii $a_d = 5 \text{ Å}$ and $a_d = 80 \text{ Å}$, with $a_d/\lambda = 1/10$ (for the greatest dielectric effect, whilst still respecting the conditions of the smoothing approximation). Since there are two data sets for each value of $\phi^r_d$, the results have been plotted separately for the sake of clarity. Like the permittivity, $\phi^r_d$ changes $A$, rendering the lower limit solutions different for each value.

Similar comments to those made about the dielectric contrast apply to these results. As $\phi^r_d$ is decreased from 0.4 to 0.1 Fig. 4.12 (top to bottom), the effect of the spheres gradually disappears.

For $\phi^r_d = 0.4$ the spheres with an 80 Å radius peel off significantly from the $B = 0$ limit, at intermediate separations, but this tendency is scaled down for smaller
Figure 4.12: Study of the effect of $\phi_d^g$ variation the shape of the pressure profiles. From top to bottom: $\phi_d^g = 0.1$, $\phi_d^g = 0.2$ and $\phi_d^g = 0.4$. The numerical data has been obtained using the values of Table 4.1.
volume fractions, so that the $B = 0$ limit is an increasingly good approximation. The use of the uniform dielectric mixture limit to describe the "real" MDH behaviour of $a_d = 5 \text{Å}$ spheres is a very good approximation for $\phi^*_d = 0.4$ and an excellent one for the smaller volume fractions.

4.5.5 Osmotic Pressure Profiles, Unequal Surface Potentials

Effect of Surface Potential Asymmetry

We conclude the present study with a sample of pressure profiles obtained using asymmetric surface potential boundary conditions, (4.32) and (4.33). The effect of decreasing the value of the "right hand surface" surface potential $W_{s2}$, measured in fractions $f$ of the near side potential, is studied, as is shown in Fig. 4.13 (top to bottom).

The pressure has a turnaround and goes negative for $D \sim \lambda$ denoting an attraction between the surfaces. This stems from electrostatic stress contributions of Equation (4.35), which are always attractive (see Equation (4.22) of Section 4.3.4). The turnaround occurs when the electrostatic attraction between the surfaces becomes comparable to the osmotic repulsion.

Decreasing the potential at the right hand surface (at $X = H$) decreases the overall size of the turnaround "hump" and moves its peak to slightly larger $H$. The pressure is, as previously, intermediate between the $A = 0$ and $B = 0$ limits, however we see that in this case at small $H$ all solutions match the $A = 0$ analytic limit, whilst at large $H$ they match the $B = 0$ solution. For intermediate values of $H$ the profile lies between the limits and we notice the position of the barrier's peak is between the two.

This behaviour is not as easily explained as for the symmetric case, though it is clearly (and trivially!) a result of the competition between the osmotic and electrostatic contributions to the pressure. In the absence of spheres, we can
Figure 4.13: Pressure profiles for unequal $W_s$: effect of decreasing the "right hand surface" potential $W_s(H)$. From top to bottom: $W_s(H) = 0.8$, $W_s(H) = 0.6$ and $W_s(H) = 0.4$ (with $W_s(0) = 1$ for all plots). The numerical data has been obtained using the values of Table 4.1.
consider the attraction as originating from the electrostatic attraction between the surface charges and any counterions condensed onto the opposite surface, screened by the presence of the free salt ions and counterions. The condensation occurs to keep the surface potential fixed, as required by the boundary conditions. For equal surface potentials, the condensation is symmetric, so that the attraction between the surfaces cancel out (in a mean field description). In the case of unequal potentials, however, for a given separation, more condensation will have occurred on the surface with a lower $V_s$, to maintain this lower potential, which entails a non zero electrostatic attraction.

When spheres are also present in solution, the situation is not so clearly explainable. We suspect they act a little like a salt, reducing the attraction between the surfaces. At any rate, the spheres contribute a repulsive electrostatic term (on top of the attractive one, to which they contribute indirectly through their effect on the field), acting to increase the pressure (see Equation (4.22)).

### 4.6 Summary and Concluding Comments

The simple model presented in this chapter already seems capture some of the effects of electrostatic coupling of solutes to surfaces. In particular, in the case of flat parallel double layers with constant surface potential, we can summarise the following:

- If large enough, the nonuniform field of a double layer can electrostatically deplete dielectric spheres from its surface in a manner which depends on the relative magnitude of the electrostatic energy of the spheres with respect to their thermal energy.

- Conversely, the dipoles induced on the spheres reduce the electrostatic energy of the double layer field, acting a little like a "dipolar" electrolyte.
• For significant dielectric contrast, this dielectric screening acts to reduce the osmotic repulsion normally present between charged plates. The reduction is more pronounced where there is more dielectric material. Thus where the depletion is least efficient at removing dielectric material, the pressure is most reduced.

• In the limits of a pure electrolyte or of a uniform dielectric mixture (immobile spheres), exact expressions for the fields of the potential, field etc., and for the osmotic pressure can be derived for the simple parallel plane geometry studied. These limits bracket the “actual” behaviour of dielectric spheres and correspond to setting the characteristic constants of the problem $A$ and $B$ (as defined in Section 4.4.2) respectively to zero.

• As expected from the order of magnitude of $A$ and $B$, increasing dielectric contrast and sphere concentration enhances the dielectric screening of the potential, reducing the overall magnitude of the osmotic pressure with respect to that of a pure electrolyte; whilst increasing surface potential, dielectric contrast and sphere volume, and decreasing the Debye length increases the sphere depletion, which makes the pressure closer to that of a pure electrolyte.

• In the case of asymmetric surface potentials, the pressure can become attractive, as for the pure electrolyte case. The presence of spheres alters the pressure profiles, whose behaviour is intermediate between the same limits as the symmetric case. It is harder to explain the observed behaviour in this case, though we know from the general expression of the pressure that the spheres contribute a repulsive contribution to the pressure, acting in a similar way to the salt.

As it stands, the present description is quite unrealistic. It may be able to qualitatively describe the long-distance osmotic interaction between charged surfaces confining dilute, large spherical dielectric solutes, such as microemulsion droplets.
This system is likely to be experimentally realisable, but even the experiment itself would represent a substantial idealisation. Given the interesting results of this chapter, however, it makes sense to extend the model to more realistic systems, as we will see in Chapter 5, making both the theory and the potential experiments more interesting.
CHAPTER 4. MODEL I: DIELECTRIC SPHERES
Model II: Dielectric Polymers

Model I (Chapter 4) is here extended to describe charged surface interactions when they reside in a solution of polymer–like molecules. Polymer solutions were chosen for two main reasons. From a theoretical viewpoint, their description is well established and existing theoretical tools can be borrowed to couple the polymer behaviour to the electrostatics. Experimentally, our choice is justified by the fact that, as we saw in Chapter 3, polymers are often mixed between the surfaces of macroions, such as those of charged lamellar phases or colloids. (In Chapter 6, we will map the model about to be described onto polymer–doped lamellar phases).

The structure of this chapter is similar to Chapter 4: the model and its approximations are described, the main equations are derived, and their solutions and predicted osmotic pressure profiles are finally presented. The physics in this chapter however is subtler and more interesting.

5.1 Model Setup and Approximations

The model is an extension of the one presented in the previous chapter. We consider here the same physical situation, shown in Fig. 5.1A: a solution of low
permittivity solutes are dissolved in an electrolyte sandwiched between charged surfaces. The electrolyte is, as in Chapter 4, an ideal solution of ions; this time, however, the solutes are polymers.

Using the Flory–Huggins mean field model (Section 2.3.1), we shall approximate the polymers as a series of random walks on a lattice, chosen, for simplicity, to be a cube of side $a_{FH}$ (the lattice length). Each polymer has $N$ monomers occupying the lattice sites; the total fraction of lattice occupied by the monomers is denoted by $\phi$, the monomer volume fraction. The rest of the lattice, $1 - \phi$, is occupied by solvent molecules. The effective interactions of the monomers with each other and with the solvent are absorbed in the $\chi$ parameter of the solution. In addition, to realistically describe the concentration correlations when a polymer solution is perturbed by an external field (e.g. a confining wall or an electric field, as in Model I) we have used the square gradient approximation (SGA) of Section 2.3.2.

To model the dielectric properties of the polymers, we assign a spherical dielectric volume (the spheres of Model I) to each monomer, as shown in Fig. 5.1B.

Our model is subject to the approximations of both Model I and the Flory–Huggins theory of polymer solutions. In particular, for the smoothing approximation of Model I to apply, we require the radius of a “dielectric monomer” $a_d$ to be much smaller than the Debye length ($a_d \ll \lambda$). Further, a Flory–Huggins treatment means our description does not apply to dilute polymer solutions, and is quantitatively accurate only for concentrated solutions.

We will ignore any electrostatic contribution to the monomer interactions (the $\chi$ parameter is the same as that of the solvent without the ions), except for indirect contributions which enter through the dielectric coupling of the polymer to the electric field. In addition, to avoid having to consider non-electrostatic interactions with the surface, we assume that the polymer does not adsorb onto any confining surfaces (monomers are excluded at contact from the surface). Finally, use of the square gradient approximation requires externally induced concentration variations, and so the inducing external fields, to be slowly varying.
5.1. MODEL SETUP AND APPROXIMATIONS

Figure 5.1: The situation to model: an ionic solution of nonadsorbing neutral polymers between charged plates. We approximate the polymer solution using the Flory–Huggins lattice model and attaching dielectric spheres to the lattice monomers, as discussed in the text. For simplicity we chose a cubic lattice, here represented by a two dimensional square lattice.

5.1.1 Relation between Lattice and Dielectric Units

The polymers are approximated by a series of dielectric spheres attached to the sites of a cubic lattice. We address here the relation between the different sizes associated with these distinct geometries.

The dielectric properties of the polymer depend on how many "oily" hydrocarbon groups are contained in every chemical monomer; the groups may be part of the polymer backbone, or side groups. A lattice length usually spans over a few chemical monomers, because the polymer chains are forced to adopt the lattice geometry (see Appendix V of [97]).

In general, we expect the radius $a_d$ of a dielectric sphere associated with a lattice monomer to differ in size from the lattice length in a nontrivial way, which will be discussed in more detail in Section 5.5.3. This difference will be described by a factor $f$ so that $a_d = a_{FH}/f$, where $a_{FH}$ is the lattice length (see Fig. 5.2).
Implications for Volume Fractions

The two different sizes discussed above entail two different volume fractions: the dielectric volume fraction $\phi_d$, $\epsilon_e = \epsilon_e(\phi_d)$, on which the effective permittivity of the solution depends, and the polymer volume fraction $\phi$ which determines the solution free energy and will be used as a variable of the problem (see Section 5.2).

The relation between the volume fractions is simple. The polymer volume fraction of chains of length $N$ in a solution of volume $V$ is defined as: $\phi \equiv (N/V)a_{FH}^3$, whilst the dielectric volume fraction is $\phi_d \equiv (N/V)4/3\pi a_d^3$. Thus, since $a_d = a_{FH}/f$, the volume fractions are related by a factor $F \equiv (4/3)\pi/f^3$:

$$\phi_d = F\phi$$  \hspace{1cm} (5.1)

The Maxwell–Garnett Relation for Polymers

To model the effective permittivity of the polymer solution, the full form of the Maxwell–Garnett Equation (2.42) will be used, since we are potentially interested in investigating concentrated systems. Recall (2.42) has the following form:
where $K = (\epsilon_1 - \epsilon_2)/(2\epsilon_1 + \epsilon_2)$. In view of the considerations of the previous subsection, (2.42) needs to be modified to be a function of the polymer volume fraction. By Equation (5.1) we have:

$$
\epsilon_\sigma(\phi_d) = \epsilon_1 \left( 1 - \frac{3K\phi_d}{1 + K\phi_d} \right)
$$

(5.2)

5.1.2 Thermodynamic Setting

We adopt the same thermodynamic point of view as in Chapter 4: the system is imagined in contact with a reference reservoir of ions and, this time, a polymer solution (Fig. 5.3). The natural thermodynamic potential for such a system is the grand potential, $\Omega(V, T, \mu_i, \mu_p)$, which is minimised at equilibrium.

Figure 5.3: The thermodynamic setting of our model: the system is in contact with a reservoir with which heat, ions and polymers can be exchanged.
5.2 Variational Formulation

The formalism employed here is identical in spirit to that used in Chapter 4: a free energy functional is minimised to obtain the “equations of motion” and the stress of the system. The problem is once more formulated variationally, by defining a “free energy action”:

\[
A_\Omega = \int_V a_\Omega(r) \, dr
\]  

(5.3)

where

\[
a_\Omega(r) = a_{el}(r) + a_{ions}(r) + a_{poly}(r)
\]  

(5.4)

is the action density whose contributions have been split into its electrostatic, ionic and polymeric. As previously, the electrostatic term reads:

\[
a_{el}(r) = \sum_{i=+, -} n_i q_i V - \frac{1}{2} \epsilon_e(\phi)(\nabla V)^2
\]  

(5.5)

where, in this case \(\epsilon_e(\phi)\) is given by Equation (5.2). The ionic contribution is:

\[
a_{ions}(r) = T \sum_{i=+, -} n_i (\ln n_i - 1) - \sum_{i=+, -} \mu_i n_i
\]  

(5.6)

The second term of (5.6) ensures conservation of each of the ionic species, since we operate in a grand canonical ensemble. All symbols of (5.6) and (5.5) are as defined in Chapter 4. The polymer contribution is given by the local Flory–Huggins free energy\(^1\), with a square gradient term modelling nonlocal correlations between polymers:

\(^1\)Note that the ideal contribution to the free energy differs here from the standard Flory–Huggins expression by an extra term \(\phi/N\) (we follow the convention of [98]). The term is linear in \(\phi\), and so is inconsequential to any derived quantity.
\[ a_{\text{poly}}(r) = T \frac{N}{a^3} \left[ \frac{\phi}{N} \ln \frac{\phi}{N} - 1 \right] + \frac{(1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi) - \frac{\mu_p}{T} \phi}{36a} \]

where from now on the lattice length is denoted the less cumbersome notation \( a \) (\( a_{FH} \equiv a \)), \( \mu_p \) is the chemical potential of the polymers in solution, ensuring their number is also conserved and all other symbols have been previously defined. The choice of the coefficient of the square gradient term is motivated by the derivation presented in Section 2.3.2.

It is Equation (5.7) which encodes the difference between the previous model and the current one: it describes polymers (see Sections 2.3.1 and 2.3.2). In addition, when compared to the "ideal gas" of spheres of Chapter 4, (5.7) provides a more realistic description of the non-electrostatic contributions to the free energy. In fact it realistically includes: excluded volume effects (the second and third terms in the square bracket), correlations between different monomers in the solution (the square gradient piece) and the applicability to concentrated solutions and near-theta point conditions (because of the second term in the square bracket). It is for the latter reason that the Flory–Huggins free energy was used and not a virial expansion.

The square gradient piece deserves particular attention. Its presence entails that the (dielectric) monomer concentration is no longer local, so that the influence of electric field or the confining effect of the wall will be felt at the midplane of a symmetric surface geometry, allowing in principle, the concentration to fall below the reservoir value. This would cause a net attraction to arise, which would not possible in Model I, as explained in Section 4.5.4.
5.2.1 Derivation of the Model’s Equations

The derivation of the differential equations describing the new model shall proceed variationally, as in Chapter 4. For this purpose it is convenient to write Equation (5.3) in its full splendour (1):

\[
\mathcal{A}_\Omega[V, n_i, \phi_d] = \\
= \int_V a_\Omega(V, n_i, \phi_d) \, d\mathbf{r} = \\
= \int_V \left( -\frac{1}{2} \varepsilon_0 (\phi_d) \nabla V \right)^2 + \sum_{i=+,-} n_i q_i V + \frac{1}{\beta} \sum_{i=+,-} n_i (\ln n_i - 1) + \\
+ \frac{T}{a^3} \left[ \frac{\phi}{N} (\ln \frac{\phi}{N} - 1) + (1 - \phi) \ln(1 - \phi) + \chi \phi (1 - \phi) \right] + \frac{T}{36a} \frac{(\nabla \phi)^2}{\phi} + \\
- \sum_{i=+,-} \mu_i n_i - \mu_p \frac{\phi}{a^3} \right) \, d\mathbf{r}
\]

Equation (5.8) is minimised by finding its null variations with respect to the fields of the problem. Performing a variation with respect to the electrostatic potential, we set: \( \delta \mathcal{A}_\Omega / \delta V = 0 \) or, equivalently, \( \frac{\partial \mathcal{A}_\Omega}{\partial V} - \nabla \frac{\partial \mathcal{A}_\Omega}{\partial V} = 0 \). From this we recover the Maxwell equation equation (4.11):

\[
\nabla (\varepsilon_0 (\phi) \nabla V) = - \sum_{i=+,-} n_i q_i
\]

where \( \varepsilon_0 (\phi) \) is given by Equation (5.2) multiplied by the permittivity of vacuum, \( \varepsilon_0 \), which for convenience we have set to 1 as in the Chapter 4.

Similarly a variation with respect to the ion number density \( \delta \mathcal{A}_\Omega / \delta n_j = 0 \), i.e. \( \frac{\partial \mathcal{A}_\Omega}{\partial n_j} - \nabla \frac{\partial \mathcal{A}_\Omega}{\partial n_j} = 0 \) yields the Boltzmann factor for ion concentrations (4.12):

\[
n_i = n_i^e e^{-q_i V/T}
\]
where, as in Model I, \( n_i^r = e^{-\mu_i/T} \) defines the chemical potential \( \mu_i \) of ion \( i \), fixed by the reservoir. All symbols in (5.2.1) and (5.2.1) have also been previously defined in Model I.

### The Polymer Equation

Finally, a variation with respect to the polymer volume fraction \( \delta A_\Omega / \delta \phi = 0 \), i.e. \( \delta a_\Omega / \delta \phi - \nabla \delta a_\Omega / \nabla \phi = 0 \), yields the differential equation for the polymer concentration:

\[
- \frac{1}{2} \frac{d e_e}{d \phi} (\nabla V)^2 + \frac{T}{a^3} \left[ \frac{1}{N} \ln \frac{\phi}{N} - \ln(1 - \phi) - 1 + \chi - 2\chi \phi - \frac{\mu_p}{T} \right] + \frac{T}{36a} \left[ \left( \frac{\nabla \phi}{\phi} \right)^2 + 2\nabla \left( \frac{\nabla \phi}{\phi} \right) \right] = 0 \tag{5.9}
\]

This equation describes the response of the polymer concentration to perturbations by electric fields and boundaries (e.g. confining hard surfaces). If such boundaries and fields are removed, we expect the system to be identical to the reservoir so that \( \phi = \phi^r \), and Equation (5.9) is simply an expression for the chemical potential. Indeed, setting \( \phi = \phi^r \) in (5.9), we find:

\[
\frac{\mu_p}{T} = \left[ \frac{1}{N} \ln \frac{\phi^r}{N} - \ln(1 - \phi^r) - 1 + \chi - 2\chi \phi^r \right] \tag{5.10}
\]

In addition, since the following identity holds:

\[
\left( \frac{\nabla \phi}{\phi} \right)^2 + 2\nabla \left( \frac{\nabla \phi}{\phi} \right) = - \left( \frac{\nabla \phi}{\phi} \right)^2 + 2 \frac{\nabla^2 \phi}{\phi}
\]

a substitution of (5.10) into Equation (5.9) yields:

\[
- \frac{1}{2} \frac{d e_e}{d \phi} (\nabla V)^2 + \frac{T}{a^3} \left[ \frac{1}{N} \ln \left( \frac{\phi}{\phi^r} \right) - \ln \left( \frac{1 - \phi}{1 - \phi^r} \right) - 2\chi(\phi - \phi^r) \right] + \frac{T}{36a} \left[ 2 \frac{\nabla^2 \phi}{\phi} - \left( \frac{\nabla \phi}{\phi} \right)^2 \right] = 0 \tag{5.11}
\]
At this point it is also convenient to differentiate the Maxwell–Garnett relation (5.2) to make the electrostatic coupling term \( (1/2)d\varepsilon_e/d\phi(\nabla V)^2 \) of Equation (5.11) explicit:

\[
\frac{d\varepsilon_e}{d\phi} = -\frac{3KF\varepsilon_1}{(1 + KF\phi)^2} \tag{5.12}
\]

And finally, to simplify the mathematical form of Equation (5.11) we will change the polymer variable to \( \psi \equiv \phi^{1/2} \) (that is \( \psi^2 = \phi \)), as conventional in (theoretical) polymer physics literature [15, 48]. This change of variables allows the simplification: \( 2\nabla^2\phi/\phi - (\nabla\phi/\phi)^2 = 4\nabla^2\psi/\psi \).

Thus, if we re-express (5.13) as a function of \( \psi \):

\[
\frac{d\varepsilon_e}{d\psi} = -\frac{3KF\varepsilon_1}{(1 + KF\psi^2)^2} \tag{5.13}
\]

(5.11), as an equation in \( \psi \), reads:

\[
\frac{1}{2}\frac{3KF\varepsilon_1}{(1 + KF\psi^2)^2}(\nabla V)^2 + \frac{T}{a^3} \left[ \frac{1}{N} \ln \left( \frac{\psi^2}{\psi^2 r^2} \right) - \ln \left( \frac{1 - \psi^2}{1 - \psi^2 r^2} \right) - 2\chi(\psi^2 - \psi^2 r^2) \right] + \frac{T}{9a} \frac{\nabla^2\psi}{\psi} = 0
\]

or rearranging:

\[
\frac{a^2}{9} \nabla^2\psi = \frac{3K\varepsilon_1 F a^3}{2T} (\nabla V)^2 \frac{\psi}{(1 + KF\psi^2)^2} + \frac{\psi}{N} \ln \left( \frac{\psi^2}{\psi^2 r^2} \right) - \psi \ln \left( \frac{1 - \psi^2}{1 - \psi^2 r^2} \right) - 2\chi(\psi^3 - \psi^2 r^2\psi)
\]

5.2.2 "Equations of Motion"

The Maxwell equation, the ion Boltzmann factor and the polymer equation just derived completely describe the system we are modelling. We summarise them again here:
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\[ \nabla (\varepsilon(e^\psi) \nabla V) = - \sum_{i=+,-} n_i q_i \]

\[ n_i = n_i^0 e^{-q_i V/T} \]  \hspace{1cm} (5.14)

\[ \frac{a^2}{9} \nabla^2 \psi = 3 \frac{K \varepsilon_1 F^3}{2 T} (\nabla V)^2 \frac{\psi}{(1 + K \psi^2)^2} + \]

\[ + \frac{\psi}{N} \ln \left( \frac{\psi^2}{\psi r_2} \right) - \psi \ln \left( \frac{1 - \psi^2}{1 - \psi r_2} \right) - 2 \chi(\psi^3 - \psi r^2 \psi) \]  \hspace{1cm} (5.15)

where \( \varepsilon(e^\psi) = \varepsilon_1[1 - 3KF\psi^2/(1 + K\psi^2)] \), the Maxwell–Garnett formula as a function of \( \psi \).

Equation (5.15) can be incorporated into (5.14), reducing the above set to the following two coupled differential equations:

\[ \nabla (\varepsilon(e^\psi) \nabla V) = - \sum_{i=+,-} n_i^0 q_i e^{-q_i V/T} \]  \hspace{1cm} (5.16)

\[ \frac{a^2}{9} \nabla^2 \psi = 3 \frac{K \varepsilon_1 F^3}{2 T} (\nabla V)^2 \frac{\psi}{(1 + K \psi^2)^2} + \]

\[ + \frac{\psi}{N} \ln \left( \frac{\psi^2}{\psi r_2} \right) - \psi \ln \left( \frac{1 - \psi^2}{1 - \psi r_2} \right) - 2 \chi(\psi^3 - \psi r^2 \psi) \]  \hspace{1cm} (5.17)

Equation (5.16) is the Poisson–Boltzmann equation with a polymer concentration dependent (and so non–constant) permittivity, as in Chapter 4. Equation (5.17) doesn’t have a name, as far as we know. A functional similar to that leading to this equation has, however, been recently derived to describe polyelectrolyte adsorption on a charged surface (see section 6 of the contribution by Khokhlov to [39]). Like the latter, Equations (5.16) and (5.17) describe the concentration variations of a polymer solution next to a charged wall. However, since we are not modelling charged polymers, the polymer profile described by (5.17) is only electrostatically affected because of the dielectric nature of the polymers (described by the first term on the right hand side of (5.17), which derives from the
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Maxwell–Garnett relation for the permittivity). Conversely in Equation (5.17), the effect of the polymer enters only through the modified permittivity.

The focus on dielectric effects, together with an extended exploration of their consequences (see Section 5.5 and Chapter 7), represent the original content of this thesis.

5.2.3 Osmotic Pressure

As before, the free energy action density does not explicitly depend on position. This allows us to define a conserved quantity which we shall once more identify with osmotic pressure. As in Chapter 4 let:

$$\Pi = \sum_m p_m \nabla Q_m - a_\Omega$$

(5.18)

where $a_\Omega$ is the free energy action density (5.4), and $Q_m$ and $p_m := \frac{\partial a_\Omega}{\partial Q_m}$ are the generalised coordinates and momenta of the problem. Recalling that $a_\Omega$ takes the form given by Equations (5.4)–(5.7):

$$a_\Omega = -\frac{1}{2} \epsilon(\phi)(\nabla V)^2 + \sum_{i=+,\,,-} n_i q_i V + T \sum_{i=+,\,,-} n_i (\ln n_i - 1) +$$

$$+ \frac{T}{a^3} \left[ \frac{\phi}{N}(\ln \frac{\phi}{N} - 1) + (1 - \phi) \ln(1 - \phi) + \chi_\phi(1 - \phi) - \frac{\mu_p}{T} \right] + \frac{T}{36a} \frac{(\nabla \phi)^2}{\phi} +$$

$$- \sum_{i=+,\,,-} \mu_i n_i$$

the generalised momenta are:

$$p_{n_i} = \frac{\partial a_\Omega}{\partial \nabla n_i} = 0$$

(5.19)

$$p_\phi = \frac{\partial a_\Omega}{\partial \nabla \phi} = \frac{2T}{36a} \frac{(\nabla \phi)^2}{\phi}$$

(5.20)

$$p_V = \frac{\partial a_\Omega}{\partial \nabla V} = -\epsilon(\phi_d) \nabla V$$

(5.21)
so that by (5.18) we can define the following quantity:

\[
\Pi = p_v \nabla V + p_\phi \nabla \phi - a_\Omega = \\
- \frac{1}{2} \varepsilon_e(\phi)(\nabla V)^2 - \sum_{i=+,,-} n_i q_i V - T \sum_{i=+,,-} n_i (\ln n_i - 1) + \sum_{i=+,,-} \mu_i n_i + \\
- \frac{T}{a^2} \left[ \frac{\phi}{N} (\ln \frac{\phi}{N} - 1) + (1 - \phi) \ln(1 - \phi) + \chi_1 (1 - \phi) - \frac{\mu_p}{T} \right] + \frac{T}{36a} \frac{(\nabla \phi)^2}{\phi}
\]

which, upon substitution of (5.10) for the polymer chemical potential, becomes:

\[
\Pi = -\frac{1}{2} \varepsilon_e(\phi)(\nabla V)^2 - \sum_{i=+,,-} n_i q_i V - T \sum_{i=+,,-} n_i (\ln n_i - 1) + \sum_{i=+,,-} \mu_i n_i + \\
- \frac{T}{a^2} \left[ \frac{\phi}{N} (\ln \frac{\phi}{\phi^r} - 1) - \phi \ln \left( \frac{1 - \phi}{1 - \phi^r} \right) + \chi_1 (2\phi^r - \phi) + \phi + \ln(1 - \phi) \right] + \\
+ \frac{T}{36a} \frac{(\nabla \phi)^2}{\phi}
\]  

(5.22)

Now, replacing the ion densities \( n_i \) with the Boltzmann factors (5.15), (5.22) reduces this to an equation in \( V \) and \( \psi \):

\[
\Pi = -\frac{1}{2} \varepsilon_e(\phi)(\nabla V)^2 - \sum_{i=+,,-} n_i^r e^{-q_i V/T} q_i V + \\
- T \sum_{i=+,,-} n_i^r e^{-q_i V/T} (\ln n_i^r - q_i V/T - 1) + T \sum_{i=+,,-} n_i^r e^{-q_i V/T} \ln n_i^r + \\
- \frac{T}{a^2} \left[ \frac{\phi}{N} (\ln \frac{\phi}{\phi^r} - 1) - \phi \ln \left( \frac{1 - \phi}{1 - \phi^r} \right) + \chi_1 (2\phi^r - \phi) + \phi + \ln(1 - \phi) \right] + \\
+ \frac{T}{36a} \frac{(\nabla \phi)^2}{\phi}
\]  

(5.23)

where we have used \( \mu_i \equiv T \ln n_i^r \). (5.23) can be finally simplified to:
\[ \Pi = \frac{1}{2} \varepsilon(\phi)(\nabla V)^2 + T \sum_{i=+,-} n_i \phi^{-q_i V/T} + \]
\[ - \frac{T}{a^3} \left[ \frac{\phi N}{\phi^r} (\ln \frac{\phi}{\phi^r} - 1) - \phi \ln \left( \frac{1 - \phi}{1 - \phi^r} \right) + \chi \phi(2\phi^r - \phi) + \phi + \ln(1 - \phi) \right] + \]
\[ + \frac{T}{36a} (\nabla \phi)^2 \]

As in Chapter 4, we interpret Equation (5.24) as the magnitude of the total stress normal to a surface placed in the solution and oriented against the force exerted on it. Once more, the stress has electrostatic (first term) and osmotic contributions (second and third terms). In addition, there is a square gradient contribution to the pressure which arises from the "push" of nearby monomers on those at the location of the surface. In the next subsections we will show how the reservoir and the net pressure can be found from (5.24).

**Recovering the Pressure of the Reservoir**

In the reservoir we have an ideal ionic solution mixed with a Flory–Huggins polymer solution, and no net field contributions. When evaluated in the "reservoir limit" (as we did when deriving the chemical potential), we thus expect the osmotic pressure (5.24) to reduce to the sum of Van't Hoff ideal contribution for the ions and a Flory–Huggins pressure term for the polymer solution. Setting \( V = 0 = \nabla V \) and \( \phi = \phi^r \), (5.24) becomes:

\[ \Pi' = T \sum_{i=+,-} n_i^r + \frac{T}{a^3} \left[ \frac{\phi^r}{N} - \chi \phi^r^2 - \phi^r - \ln(1 - \phi^r) \right] \]

Equation (5.25) agrees with our expectations and is an expression for the reservoir pressure. It also provides a check of our derivation of the osmotic pressure as a conserved quantity, since the polymer contribution to Equation (5.25) can be independently and directly derived by differentiation of the Flory–Huggins free energy of a bulk polymer solution (e.g.: see section III.1.3 of Reference [15]).
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5.2.4 Net Osmotic Pressure

To find the net "interaction" between the plates, we will subtract the reservoir pressure (5.25) from the total pressure (5.24), as we did for Model I:

\[
\Pi^{net} = \Pi - \Pi' = \left\{ -\frac{1}{2} \epsilon_e (\phi) (\nabla V)^2 + T \sum_{i=+,-} n_i e^{-q_i V / T} + \right. \\
- \frac{T}{a^3} \left[ \frac{\phi}{N} \ln \frac{\phi}{\phi^*} - 1 \right] - \phi \ln \left( \frac{1 - \phi}{1 - \phi^*} \right) + \chi \phi (2\phi^* - \phi) + \phi + \ln(1 - \phi) + \\
+ \frac{T}{36a} \left( \nabla \phi \right)^2 \left\{ \frac{\phi^*}{N} - \chi \phi^* \left[ \frac{\phi^*}{N} - \phi^* - \ln(1 - \phi^*) \right] \right\}
\]

which can be simplified to:

\[
\Pi^{net} = -\frac{1}{2} \epsilon_e (\phi) (\nabla V)^2 + T \sum_{i=+,-} n_i e^{-q_i V / T} - 1 + \left( \frac{\phi}{N} \ln \frac{\phi}{\phi^*} + \frac{\phi^* - \phi}{N} \right) + (1 - \phi) \ln \left( \frac{1 - \phi}{1 - \phi^*} \right) - \chi (\phi^* - \phi)^2 - (\phi^* - \phi) + \\
+ \frac{T}{36a} \left( \nabla \phi \right)^2
\]

This is the net osmotic pressure between the plates. Once the solutions of the model's equations \((V \text{ and } \phi \equiv \psi^2)\) is known for a given separation, a substitution into (5.27) yields the osmotic pressure. Again, we will exploit the "conservation of \(\Pi\)" for a given system volume, to make the evaluation of (5.27) convenient.

5.3 Monovalent Ions

As mentioned in Section 2.2.4 (and shown in Figures 4.6 and 4.7), for large surface potentials, the Debye–Hückel approximation does not provide a physical
description of the ion distributions about a charged surface. In such situations, a realistic description (in view of later developments, such as the description of lamellar phases with high surface charges) requires a full Poisson–Boltzmann approach, as just derived.

It is possible, however, to simplify the mathematical form of the rather "ugly" Equation (5.16) by assuming the counterions and electrolyte ions are monovalent. This is not a very restrictive assumption, as many experimentally employed electrolytes consist of monovalent ions.

Monovalent ions have (by definition) unit valency, and thus positive and negative ions respectively carry charges \( q_+ = e \) and \( q_- = -e \). The reservoir density is the same for both species and is equal to the number density of dissolved electrolyte ions \( n_+ = n_- = n'_r \). Substituting these values into the right hand side of Equation (5.16), it becomes:

\[
\nabla (\varepsilon_e(\psi) \nabla V) = -\frac{e}{\varepsilon_1} n'_r (e^{-eV/T} - e^{-eV/T})
\]

or, using the definition of sinh and multiplying both sides by \( e/T \):

\[
\nabla [\varepsilon_e(\psi) \nabla(eV/T)] = \kappa^2 \sinh(eV/T)
\]

where \( \kappa \equiv 1/\sqrt{8\pi l_B n'_r} \) is the inverse Debye length for a monovalent salt of number density \( n'_r \) (\( l_B = q^2/4\pi\varepsilon_1 T \) is the Bjerrum length of Section 2.2.1) and we have rescaled the Maxwell–Garnett formula by the solvent permittivity, so that \( \varepsilon_e(\psi) = \varepsilon_e/\varepsilon_1 = [1 - 3KF\psi^2/(1 + KF\psi^2)] \).

The differential equations of our model now read (renumbering the polymer equation for convenience):

\[
\frac{a^2}{9} \nabla^2 \psi = \frac{3K\varepsilon_1 Fa^3}{2T} (\nabla V)^2 \frac{\psi}{(1 + KF\psi^2)^2} + \frac{\psi}{N} \ln \left( \frac{\psi^2}{\psi^2_{r2}} \right) - \psi \ln \left( \frac{1 - \psi^2}{1 - \psi^2_{r2}} \right) - 2\chi(\psi^3 - \psi^2_{r2})
\]

\[
\nabla[\varepsilon_e(\psi) \nabla(eV/T)] = \kappa^2 \sinh(eV/T)
\]

\[
\frac{a^2}{9} \nabla^2 \psi = \frac{3K\varepsilon_1 Fa^3}{2T} (\nabla V)^2 \frac{\psi}{(1 + KF\psi^2)^2} + \frac{\psi}{N} \ln \left( \frac{\psi^2}{\psi^2_{r2}} \right) - \psi \ln \left( \frac{1 - \psi^2}{1 - \psi^2_{r2}} \right) - 2\chi(\psi^3 - \psi^2_{r2})
\]
5.3. MONOVALENT IONS

The same substitutions as above apply to the osmotic pressure, (5.27):

\[ \Pi^{net} = -\frac{1}{2} \varepsilon_e(\phi)(\nabla V)^2 + 2n_sT(e^{-eV/T} + e^{eV/T} - 1) + \ldots \] [Polymer Terms] \hspace{1cm} (5.30)

and, since \( \cosh(x) \equiv (e^x + e^{-x})/2 \) and using the hyperbolic identity: \( \sinh^2(x) = (\cosh(2x) - 1)/2 \) we can write (5.30) as:

\[ \Pi^{net} = -\frac{1}{2} \varepsilon_e(\phi)(\nabla V)^2 + 4n_sT \sinh^2 \left( \frac{eV}{2T} \right) \]

\[ \frac{T}{a^3} \left[ \frac{1}{N} \ln \frac{\phi}{\phi^r} + \frac{(\phi^r - \phi)}{N} + (1 - \phi) \ln \left( \frac{1 - \phi}{1 - \phi^r} \right) - \chi (\phi^r - \phi)^2 - (\phi^r - \phi) \right] + \frac{T}{36a} \frac{(\nabla \phi)^2}{\phi} \] \hspace{1cm} (5.31)

The solution of Equations (5.28)–(5.29) for appropriate boundary conditions and calculation of the net osmotic pressure from (5.31) is the subject matter of the next section.

Debye–Hückel Limit

For weak electrostatic potentials \( (eV/T \ll 1, \text{ so that } \sinh(eV/T) \approx eV/T) \) Equation (5.28) reduces to the modified Debye–Hückel equation:

\[ \nabla (\varepsilon_e(\psi) \nabla \psi) = \kappa^2 V \] \hspace{1cm} (5.32)

where \( \varepsilon_e \) and \( \kappa \) are as previously defined, and in the same limit the osmotic pressure becomes:

\[ \Pi^{net} = -\frac{1}{2} \varepsilon_e(\phi)(\nabla V)^2 + \frac{1}{2} \varepsilon_1 \kappa^2 V^2 + \]

\[ \frac{T}{a^3} \left[ \frac{1}{N} \ln \frac{\phi}{\phi^r} + \frac{(\phi^r - \phi)}{N} + (1 - \phi) \ln \left( \frac{1 - \phi}{1 - \phi^r} \right) - \chi (\phi^r - \phi)^2 - (\phi^r - \phi) \right] + \frac{T}{36a} \frac{(\nabla \phi)^2}{\phi} \] \hspace{1cm} (5.33)
5.4 Solving the Model: Parallel Surfaces

At this stage the model needs to be formulated so that we can numerically solve its equations and from their solutions graph the predicted net pressure between surfaces. We will adopt an approach identical in spirit to that used Model I: Equations (5.28) and (5.17) will be set up to be solved for the case of parallel flat surfaces, infinite in extent, subject to appropriate boundary conditions. As before, from these solutions we can predict the net osmotic pressure between the surfaces as a function of their separation, which together with examples of the physical solutions of the model, will be presented in Section 5.5.

5.4.1 Setting Up for Solution

1D Form and Dimensionless Variables

Once more we adopt $x$ as the distance from the "left most" plate where we place our origin. This distance, and the unknown functions of the model, the potential $V$ and the square–root concentration $\psi$, are rescaled to the following values:

$$ W \equiv \frac{V}{V_0}; \quad \Psi \equiv \frac{\psi}{\psi_r}; \quad X \equiv \frac{x}{\lambda}; $$

where $V_0 \equiv T/e$ is the electrostatic potential at which an elementary charge would possess thermal energy\(^{\text{ii}}\) and $\psi_r \equiv \sqrt{\rho}$ is the square root of the reservoir monomer concentration.

With these definitions, our equations of motion become:

\(^{\text{ii}}\)Note that this is in general different from the surface potential $V_s$ of the previous chapter.
5.4. SOLVING THE MODEL: PARALLEL SURFACES

\[ \frac{d}{dX} \left( \epsilon_e(\Psi) \frac{dW}{dX} \right) = \sinh W \]  
\[ \mathcal{C} \frac{d^2 \Psi}{dX^2} = \mathcal{B} \left( \frac{dW}{dX} \right)^2 \frac{\Psi}{(1 + A \Psi^2)^2} + \frac{\Psi}{N} \ln(\Psi^2) - \Psi \ln \left( \frac{1 - \phi^r \Psi^2}{1 - \phi^r} \right) - \mathcal{D}(\Psi^3 - \Psi) \]  

where \( \epsilon_e(\Psi) = [1 - 3A \Psi^2/(1 + A \Psi^2)] \) and we have defined, for convenience, the following constants: \( A \equiv KF\phi^r, \mathcal{B} \equiv (3/2)K\epsilon_1(V_0/\lambda)^2Fa^3/T, \mathcal{C} \equiv (a/\lambda)^2/9 \) and \( \mathcal{D} \equiv 2\chi\phi^r \).

Mathematically, we are faced with the problem of finding the solutions to a set of two coupled second order differential equations, requiring the four boundary conditions laid out below. The equations are nonlinear and will be solved numerically.

**Boundary Conditions**

We require four boundary conditions arising from the constraints imposed by confining surfaces on the electrostatic and polymeric "fields".

Fixed potential and fixed surface charge boundary conditions are available approximations for the surface electrostatic behaviour (Section 2.2.2). In view of describing charged lamellar phases, whose unknown surface charge density can be crudely estimated from the area available to charged surfactant groups (Chapter 7)\(^{iii} \), we have chosen the condition of fixed surface charge.

As mentioned in Section 5.1, the polymers in solution are considered to be non-adsorbing (so as to avoid consideration of nonelectrostatic interactions with the surface). This entails a null polymer concentration at the surface.

\(^{iii} \)We saw in Section 2.2.4 how the actual surface charge, which depends on ionisation, is hard to measure.
Further, for simplicity, we will treat only the case of identical surfaces, so that the two other necessary boundary conditions follow by symmetry (and the expression for the osmotic pressure is simplified).

Mathematically, the boundary conditions express a boundary value problem: the values of the unknowns of Equations (5.34) and (5.35) are known at different positions. Formally:

\[
\left. \frac{dV}{dx} \right|_{x=0} = -\frac{\sigma}{\epsilon_1} = \left. \frac{dV}{dx} \right|_{x=D} \\
\Rightarrow \left. \frac{dV}{dx} \right|_{x=D/2} = 0
\]

\[
\psi|_{x=0} = 0 = \psi|_{x=D} \\
\Rightarrow \left. \frac{d\psi}{dx} \right|_{x=D/2} = 0
\]

Where Equation (5.36) ensures the surface field of the surfaces at \( x = 0 \) and \( x = D \) (where \( D \) is the separation between them) matches that produced by a fixed surface charge density \( \sigma \). Equation (5.38) ensures the monomer concentration at the surfaces \( s \) is zero \( \phi|_s = 0 \) (\( \Rightarrow \psi_s \equiv \sqrt{\phi}|_s = 0 \)). The symmetry of the surface properties entails that the boundary conditions at the far surface at \( x = D \) can be replaced by the requirement of vanishing derivatives at the midplane: Equations (5.37) and (5.39).

In terms of the dimensionless variables defined earlier, (5.36)–(5.39) become:
\[ \begin{align*}
\left. \frac{dW}{dX} \right|_{X=0} &= -\frac{\sigma}{\epsilon_1} = \left. \frac{dW}{dX} \right|_{X=H} \\
&\Rightarrow \left. \frac{dW}{dX} \right|_{X=H/2} = 0 \\
\psi|_{X=0} &= 0 = \psi|_{X=H} \\
&\Rightarrow \left. \frac{d\psi}{dX} \right|_{X=H/2} = 0
\end{align*} \]

where we have defined the dimensionless surface field \( F_0 \equiv \sigma \lambda / (\epsilon_1 V_0) \), \( H \equiv D/\lambda \) is the dimensionless separation between the plates, and all other symbols have been previously defined.

**Osmotic Pressure**

It is also convenient to express Equation (5.31) for the osmotic pressure in terms of dimensionless variables and constants. As in Model I, we exploit the conservation of pressure for a given separation and evaluate it at the midplane \( X = H/2 \), where the field and gradient contributions vanish. Letting \( \Phi = \Psi^2 \), (5.31) becomes, as a function of \( W(H/2) \equiv W|_{H/2} \) and \( \Phi(H/2) \equiv \Phi|_{H/2} \):

\[ \Pi^{net} = \pi_{ion}^r \sinh^2 \left( \frac{W|_{H/2}}{2} \right) - \pi_{poly}^r \left[ \frac{\Phi|_{H/2}}{N} \ln \Phi|_{H/2} + \frac{(1 - \Phi|_{H/2})}{N} \right] + \frac{(1 - \Phi|_{H/2})}{\phi^r} \ln \left( \frac{1 - \Phi|_{H/2}}{1 - \phi^r} \right) - 2 \chi(1 - \Phi|_{H/2})^2 - (1 - \Phi|_{H/2}) \]

where we have defined the constants \( \pi_{ion}^r \equiv 4n_s^r T \) and \( \pi_{poly}^r \equiv \phi^r T / a^3 \), which determine the magnitude of the ionic and polymeric contribution to the net pressure between the plates.
5.4.2 Limits, Orders of Magnitude etc.

Equations (5.34) and (5.35) are more involved than the modified Debye–Hückel equation of Model I.

To obtain the analytic solution of even the simple Poisson–Boltzmann equation for the case of parallel surfaces one has to invoke exotic functions. One might therefore assume that any limiting form of (5.34) and (5.35) is useless, since it requires the same numerical effort as the full model. Limiting forms, however, provide an important comparison with well known equations describing such limits and will be derived as a check of our model and for comparison with the previous one. In particular, the "uncoupled limit", where the coupling between the model's equations is removed, provides a useful comparison with the physics expected when the dielectric effects we are interested in are ignored.

To define some of these physical limits, it is necessary to interpret the dimensionless constants appearing in the model equations.

**Meaning of \( A, B, C \) and \( D \)**

(5.34) and (5.35) have been written in terms of the following dimensionless constants:

\[
\begin{align*}
A & \equiv K F \phi^* \\
B & \equiv (3/2)K \epsilon_1 (V_0 / \lambda)^2 F a^3 / T \\
C & \equiv (a / \lambda)^2 / 9 \\
D & \equiv 2 \chi \phi^T
\end{align*}
\]

The meaning of the above is clearer if we recall the various terms in (5.34) and (5.35), have correspondents in the energy action (5.8) and the Maxwell–Garnett relation (5.2).
\( \mathcal{A} \) appears in the Maxwell–Garnett relation and determines the reduction of the permittivity of the solution caused by the polymers as low permittivity dielectrics. The meaning of \( \mathcal{A} \) is essentially the same as \( A \) of Model I (Section 4.4.2): it represents how much the dielectric decreases the electrostatic energy.

Similarly \( \mathcal{B} \) has the same meaning as the constant \( B \) of model I: it represents the energy of polarisation of a dielectric monomer in units of \( T \). This is given by

\[
U_d = \frac{1}{2} \alpha E^2 / T,
\]

where here we identify \( \alpha = K \epsilon_1 F a^3 \), the polarisability of the monomers and \( E^2 \sim (V_0 / \lambda)^2 \), a characteristic field \(^{iv}\).

\( \mathcal{C} \) is the coefficient of the “gradient term” in the polymer equation. It measures the extent of non local perturbations on the polymer concentration. It contains the ratio of the two characteristic length scales of the problem: the lattice length \( a \) of the polymer and the Debye length in the reservoir \( \lambda \).

\( \mathcal{D} \) is a purely polymeric term representing the polymer interactions in the solution. \( \mathcal{A} \) and \( \mathcal{B} \) are responsible for the coupling between (5.34) and (5.35). If \( \mathcal{A} = 0 = \mathcal{B} \) the equations uncouple. This will happen if we use a polymer which the surface field is unable to distinguish from the solvent: \( \epsilon_1 = \epsilon_2 \ (K = 0) \). Alternatively we could use a polymer with a tiny amount of dielectric material per lattice monomer \((F = 0 \ ^v)\).

Another constant appearing in the polymer equation is the chain “length” \( N \), the number of monomers in a polymer chain. This affects the monomer entropy, but when its value is large the first term of (5.35) becomes negligible. We will briefly consider such scenarios, before considering the uncoupled limit of the full model \( \mathcal{A} = 0 = \mathcal{B} \), which is of practical interest to us.

\(^{iv}\)This field would be better characterised if we had rescaled the potential by the surface potential.

\(^{v}\)recall \( F \sim 1/f^3 \), where \( f \) represents how much larger the lattice length is with respect to the “dielectric radius”.

5.4. SOLVING THE MODEL: PARALLEL SURFACES
Small $\phi^r$, Large $N$ Limits

In the limit of low monomer concentration, $\phi^r \ll 1$, using the expansions $\ln(1 + x) = x - x^2/2 + \mathcal{O}(x^3)$ and $(1 + x^2)^{-n} = 1 - nx^2 + \mathcal{O}(x^4)$, Equations (5.34) and (5.35) become:

$$\frac{d}{dX} \left( \tilde{\varepsilon}_e(\Psi) \frac{dW}{dX} \right) = \sinh W \tag{5.45}$$

$$C \frac{d^2 \Psi}{dX^2} = B \left( \frac{dW}{dX} \right)^2 \Psi + \frac{\Psi}{N} \ln(\Psi^2) + \tilde{\nu} \phi^r (\Psi^3 - \Psi) \tag{5.46}$$

Here $\tilde{\varepsilon}_e(\Psi) = 1 - 3A\Psi^2$ is the low concentration limit of the Maxwell–Garnett equation and $\tilde{\nu} \phi^r \equiv \phi^r - D = \phi^r (1 - 2\chi)$ defines the dimensionless Flory–Huggins excluded volume parameter $\tilde{\nu}$.

For long polymers $N \gg 1$, so Equation (5.46) loses the chain entropy contribution:

$$C \frac{d^2 \Psi}{dX^2} = B \left( \frac{dW}{dX} \right)^2 \Psi + \tilde{\nu} \phi^r (\Psi^3 - \Psi) \tag{5.47}$$

Simple Model Limit

We can recover the simple model of Chapter 4 by considering the limit of ideal polymers (no interactions) of unit length in the low concentration and Debye–Hückel limits. Setting $N = 1$ and $\tilde{\nu} = 0$ in Equation (5.46) and demanding the gradient terms be negligible ($C \equiv (a/\lambda)^2/9 \ll 1$), we obtain:

$$\frac{d}{dX} \left( \tilde{\varepsilon}_e(\Psi) \frac{dW}{dX} \right) = W \tag{5.48}$$

$$\ln(\Psi^2) = B \left( \frac{dW}{dX} \right)^2 \tag{5.49}$$

which we see is equivalent, modulo a few algebraic manipulations and a different rescaling of the potential, to Equation (4.27) of Chapter 4.
5.5. RESULTS

Uncoupled Limit

As mentioned above, Equations (5.34) and (5.35) decouple if we set $A = 0 = B$:

\[
\frac{d^2 W}{dX^2} = \sinh W \quad (5.50)
\]

\[
\mathcal{C} \frac{d^2 \Psi}{dX^2} = \frac{\Psi}{N} \ln(\Psi^2) - \Psi \ln \left( \frac{1 - \phi^r \Psi^2}{1 - \phi^r} \right) - D(\Psi^3 - \Psi) \quad (5.51)
\]

The solution to (5.50) and (5.51) provide a useful reference limit to be compared with the solutions of the full model. However, they also represent the equations one might try to solve to describe a solution of uncharged polymers confined between charged surfaces, ignoring the possibility of polymer polarisation. In this frame of mind, one would simply solve the Poisson–Boltzmann equation for the electrostatics complemented by an independent description of the polymers (in our case is provided by Flory–Huggins theory with square gradients added).

A well known description of the polymers is the one derived by the method of the self–consistent fields (SCF) [15]. In the limit of long chains and small monomer concentration $(1/N \ll \phi^r \ll 1)$, we can reduce the uncoupled polymer Equation (5.51) to one identical (up to the numerical factor arising from a different use of square gradient prefactors) to that predicted by the SCF$^\text{vi}$:

\[
\frac{a^2 d^2 \Psi}{9 dx^2} = \tilde{\nu} \phi^r (\Psi^3 - \Psi) \quad (5.52)
\]

where $\tilde{\nu} \equiv (1 - 2\chi)$ and the dimensionality of the position variable has been restored.

5.5 Results

In what follows we present results in the same format as in Section 4.5. After discussing our expectations for the physics of the rather more complicated

$^\text{vi}$see e.g. equations IX.38 of [15] or 7.8 of [65].
polymer–plate system, we will present the prediction for the intra–surface physics at a given separation $H$ and then look at the effect of parameter variation on the osmotic pressure profiles. The results provide a useful comparison with Chapter 4. In addition, as we shall show in Chapter 6, from the predicted pressures it is possible to extract information about the phase behaviour of lamellar phases, as presented in Chapter 7, for which the following results furnish a useful interpretation aid.

5.5.1 Numerics

As in Chapter 4 we have used our own custom versions of standard numerical methods to solve the two coupled differential equations of the model, a detailed description of which can be found in Appendix A.

5.5.2 Expectations

The model described in this chapter now includes non–adsorbing polymers with interactions. Before discussing the results, let us discuss our expectations for the physics governing this system, which is more subtle than that of Model I. Such expectations will be of guidance in the interpretation of results.

Polymer Depletion Attraction

Let us at first ignore all electrostatic effects. We saw in Section 2.3.2 that a polymer solution can cause nonadsorbing surfaces to attract. It was also mentioned that such depletion attraction is short ranged, since the confining effect of the surfaces only extends over a screening length $\xi$. Since $\xi$ is only strictly defined in the bulk for small fluctuations (as we saw in Section 2.3.2) or when analytic solutions are possible [15], we will henceforth give it a qualitative definition: $\xi \equiv \text{"the distance over which concentration perturbations are significant"}$. When two
surfaces, in contact with a polymer reservoir, are brought together to a separation $\sim 2\xi$ the polymer solution experiences twice the entropy reduction of each surface. As the gap between the surfaces is narrowed, the cost of entropic confinement will always be greater than the osmotic work required to expel the polymer into the reservoir. This expulsion causes the pressure in the gap to fall below the reservoir value, which amounts to an attractive force between the surfaces. Finally we also define qualitative dependencies of $\xi$ (inspired by the expression (2.38)): $\xi$ is falls with increasing polymer concentration $\phi$ (more polymer more screening) and, unless we are close to the $\theta$ point of the solution, with decreasing $\chi$ parameter (the poorer the solvent, the smaller the screening).

**Electrostatic Repulsion**

Now let us consider charged surfaces in an electrolyte devoid of polymers. As we saw for the results of Section 4.5.4, in the limit of no dielectric, the surfaces will simply feel the repulsion generated by their overlapping double layers. For large separations (small electrostatic potentials between the surfaces), the electrolyte ions will enter from the reservoir screening the interactions.

**Electrically Assisted Depletion and The Coupled Case**

In reality, we expect the above effects to be complicated by the electrostatic coupling between the polymers and the charged surfaces. If the coupling were not present, we would expect the interaction between the surfaces to be the resultant of the electrostatic repulsion and, for separations below $\sim 2\xi$, the depletion attraction described above. However, as we saw in Chapter 4, the polarisation of dielectrics in a field can also cause them to deplete from charged surfaces. This effect is expected at the very least to modify the polymer expulsion (and the resulting attraction) as surfaces are brought close. In general, then, the discussion in terms of $\xi$ presented above for uncharged surfaces is no longer valid.
In Chapter 4 it was also shown how the presence of dielectric spheres reduces the electrostatic repulsion between charged surfaces; this may also be an important effect. We notice, however, that in contrast with the simple model of Chapter 4, the dielectric now has the option of being expelled, and once this is complete, the contribution to the electrostatic repulsion should be identical to that of a pure ionic solution.

We can conclude that we expect the same general behaviour as if coupling were ignored: the surfaces electrostatically repel, except if they are brought together below a critical separation, where the polymer depletion can cause the surfaces to attract. The strength and range of these surface forces is however complicated by the coupling in a way that we're going to investigate in what follows.

### 5.5.3 Parameters Used

To calculate the results of the following sections, we used the basis parameters of Table 5.1, deviating from these only to change the particular parameter under study.

The first three entries of the table are fundamental constants and the reservoir temperature \( T \) is fixed at room temperature, as for Model I (Table 4.1). The other parameters have been chosen to provide a realistic description of a typical polymer–doped lamellar phase, with a nonadsorbing polymer, such as those described in Chapter 3.

We will discuss the choice of the surface charge density \( \sigma \) and the reservoir salt concentration \( c'_s \) in relation to lamellar phases in Chapter 7. Suffice it here to say that the values shown in Table 5.1, and when \( \sigma \) and \( c'_s \) are under study in Sections 5.5.5 and 5.5.5, are not unreasonable for such doped smectics nor, more generally, for a typical "laboratory" complex fluid system.

Once more, the electrolyte is assumed to have the same permittivity as water, here \( \epsilon_1 = 78.5 \). To maximise dielectric contrast, a value of 2 (the permittivity
### Results

- **Elementary charge** $e = 1.6 \times 10^{-19}$ C
- **Permittivity of vacuum** $\varepsilon_0 = 8.85 \times 10^{-12}$ F m$^{-1}$
- **Boltzmann's constant** $k_b = 1.38 \times 10^{-23}$ J K$^{-1}$
- **Temperature** $T = 298$ K
- **Surface charge** $\sigma = 0.1$ e nm$^{-2}$
- **Res. salt concentration (Debye length)** $c_s^*(\lambda) = 0.02$ M (21.5 Å)
- **Permittivity of ionic solution** $\varepsilon_1 = 78.5$
- **Permittivity of polymer** $\varepsilon_2 = 2$
- **Dielectric factor** $f = 1.5$
- **Polymer lattice length** $a = 10$ Å
- **Flory Parameter** $\chi = 0.495$
- **Number of lattice units per chain** $N = 2000$
- **Res. monomer volume fraction** $\phi^r = 0.3$

<table>
<thead>
<tr>
<th>Table 5.1: Parameters used to solve Model II</th>
</tr>
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of hydrocarbon oils) is chosen for the polymer permittivity $\varepsilon_2$ (the same as the spheres of Model I), a value which is not unrealistic, but probably on the low side for an accurate description of aqueous polymer solutions\textsuperscript{vii}. When studying the effect of dielectric contrast on the osmotic interaction between surfaces, $\varepsilon_2$ will be varied in the range $2 - 78.5$.

The lattice length $a$ was modelled on the water soluble polymer PVP. Once a given lattice is chosen (a choice which should reflect the flexibility of the polymer to be modelled), the lattice length can be related to the monomer size of the polymer of interest, as determined from experiments. Similarly, since the total contour length of the polymer is fixed, knowledge of the the polymer molecular weight constrains the number $N$ of lattice units per chain. Such relations (see \textsuperscript{vii}Zaviansky et al.[99] have performed experiments mixing up to $\approx 50\%$ w/w PVP or PEG in H$_2$O. Their data is well fitted by $\epsilon_e = \epsilon_1(1 - \Delta c_p)$, where $\Delta$ is a constant and $c_p$ is the polymer concentration. A comparison with Equation (5.2) or its low concentration limit gives $\varepsilon_2 = 2 - 20$, depending on the model used and the value of the factor $f$ chosen.
appendix V of [97]) have been used to find $a = 10\ \text{Å}$ and $N = 2000$ for PVP with molecular weight $M_w \approx 500000$.

The estimation of $f$, the size difference between the lattice length and the radius of the dielectric sphere, is more approximate. As mentioned in Section 5.1.1, the amount of polarisable material in a polymer is determined by how much of such material is to be found in a chemical monomer. It was also mentioned how the lattice length spans several (chemical) monomers; indeed in the case of PVP, $a = 10\ \text{Å}$ is about three times as big as the length of each monomer $\approx 3\ \text{Å}$. From these considerations the value of $f = 1.5$ seems not unrealistic, if a little exaggerated, as it entails that the Flory–Huggins ("entropic") volume available to a lattice monomer, $V_{FH}$, occupies about 80% of the polarisable volume, $V_d$ ($V_{FH}/V_d \approx f^3/4 \approx 0.84$). When studying the role of $f$ itself, this value has been further exaggerated or made more realistic by using $f = 1.1$ ($V_{FH}/V_d \approx 0.33$), and $f = 2$ ($V_{FH}/V_d \approx 2$) respectively.

The choice of $x$ parameter has been made to maximise the correlations between monomers, and so the propagation of any coupling effects. For this reason the electrolyte was chosen to be a near theta solvent with $x = 0.495$. When studying the effect of changing the solvent quality, better quality (good) solvents with $x = 0.4$ and $x = 0.3$ were chosen. As mentioned in Section 5.1, any direct electrostatic contribution to $x$ was ignored. In particular, we expect the effect of the electrolyte on $x$ to be unimportant for small salt concentrations (for experiments in brine this may not be such a good approximation [82]).

Finally the reservoir monomer concentration has been fixed at a reasonably high value of $\phi^r = 0.3$. The value was chosen so that the concentration of polymer would not be too small (potentially swamping out any dielectric coupling effects) or too large (making the equations numerically hard because of strong coupling). The choice is somewhat arbitrary by nature, since $\phi^r$ is unconstrained and can, in theory, be changed at will, as we have done in Section 5.5.5, where the effects of such variation are studied.
5.5. RESULTS

5.5.4 Physical Predictions of the Model Equations

In Fig. 5.4 we show the solutions to (5.34) and (5.35) and some important derived quantities, for a spacing between the plates of $H \approx 2.37$ (recall $H$ is the plate separations in units of the Debye length in a pure electrolyte).

It is interesting to compare the features of the results of Fig. 5.4a-d with those of Model I (Figures 4.6 and 4.7). In general, we notice a qualitative similarity between the results and that the physical quantities reflect the symmetry of the boundary conditions. The electrostatic variables, the dimensionless potential $W$ and field $F^\text{viii}$ of Fig. 5.4a-b, are very similar to the those predicted by Model I. The differences in surface behaviour of $W$ and $F$, arise from the boundary conditions, since here we hold the charge density fixed and not the potential, as in Model I. Apart from this, we see that the coupled and uncoupled descriptions have the same electrostatic relation to each other as the $A = 0$ limit and the MDH equation solutions of Model I: the presence of dielectric (coupling) reduces the electrostatic potential around the midplane with respect to the uncoupled case, and the electric field is raised above the Poisson–Boltzmann description since the dielectrics act as a source of polarisation charge.

The dielectric profile is different from Model I, since we are now dealing with nonideal, polymeric dielectrics (Fig. 5.4c). As prescribed by the condition of nonadsorption at the surfaces, the monomer concentration falls to zero at the surfaces; the constraint is absent from the equivalent results of Model I. In the absence of coupling, the concentration profile is more “square” as a result of the square gradient penalty; the qualitative features of the prediction compare well with a recent theoretical and computational study of polymer chains confined in a slit [100]. The electrostatic coupling to the double layer field rounds the polymer profile off a little, for these particular parameters (see also Fig. 5.6). Comparison with the results of Model I suggests that this is a result of “electrostatic depletion”. In addition to these effects, the presence of the square gradient

\[ F^\text{viii} \equiv -dW/dX \]

\[ \text{is not to be confused with the dielectric factor } F \text{ of Section 5.1.1.} \]
contribution allows polymer to leave the space between the surfaces: we can see from Fig. 5.4c that, at the midplane, the coupled prediction is for a polymer concentration visibly below the reservoir value, unlike the uncoupled case.

The effect of the polymer concentration reflects on the permittivity profile, whose value falls from that of "pure electrolyte" at the surface (where no polymer can reach) to that of the reservoir solution as seen by the double layers (the uniform dielectric mixture limit of the previous chapter).

Figure 5.4: Variation with position of the dimensionless (a) electrostatic potential $W$, (b) electric field $F$, (c) monomer volume fraction $\Phi$ and (d) dielectric constant $\varepsilon_\alpha \equiv \varepsilon_e / \varepsilon_1$ for surfaces of separation $H \approx 2.37$. Solutions of the coupled (solid line) and uncoupled (dotted line) equations discussed in the text are shown and were found using the parameters of Table 5.1.

To conclude this brief survey of results we include a plot (Fig. 5.5), only shown in the half plane terminating at $H/2$, of the ionic profiles predicted by Model II. We see that the Poisson–Boltzmann description predicts a sensible, "asymmetric" behaviour for the ion densities (here indicated by $c_{\pm}$): the ions of opposite charge
5.5. RESULTS

to the surface are accreted on it, and those of the same sign depleted from it. Coupling raises the positive profile and lowers the negative one, analogously to the behaviour predicted by Model I.

Figure 5.5: Variation with position of the positive and negative ion profiles, rescaled by the reservoir value, for surfaces of separation $H \approx 2.88$. Solutions of coupled and uncoupled equations are shown (as labelled in the legend) and were found using the parameters of Table 5.1, except for the reservoir salt concentration and $\chi$ parameter, here changed to the values $c'_s = 0.047 M (\lambda = 14 \text{Å})$ and $\chi = 0.3$.

Polymer Expulsion

We mentioned how the characteristic difference we expect to emerge from the solutions of the model here presented is the possibility of the polymer being forced out from between the plates, and possibly causing attractive interactions. Fig. 5.6 displays the occurrence of such entropically caused expulsion due to a progressive decrease in plate separation from the solutions of the coupled equations:

We see that below a separation of $H \approx 1$ the profile goes flat and all the polymer has been expelled from between the surfaces. As we shall see this expulsion can affect the osmotic interaction between surfaces for the parameters we have chosen.
Figure 5.6: Polymer concentration profiles as the separation between surfaces is decreased. The profiles were found with the parameters of Table 5.1.
to use in this chapter. The expulsion is also predicted in the uncoupled case (not shown); the coupling however, tends to increase expulsion as shown suggested by Fig. 5.4c and as will be made evident by the results to follow.

### 5.5.5 Osmotic Pressure Profiles

From Equation (5.44), we know there are two contributions to the osmotic pressure: a repulsive electrostatic one and a polymeric one (attractive for separations below those at which the polymer starts to be expelled from between the plates). In what follows, we shall investigate the parameter dependence of the osmotic pressure profiles and show how these result from a competition between the attractive and repulsive contributions mentioned.

#### Electrostatic Parameters

**Effect of Surface Charge Density**

We start our study by varying the surface charge density $\sigma$, as shown in Fig. 5.7. For all values of $\sigma$ we notice a "wiggle" in the osmotic pressure curve, caused by the attractive polymer contribution. As $\sigma$ is decreased, so is the repulsive contribution to the osmotic pressure, so that for $\sigma = 0.05 \text{ e nm}^{-2}$ the attraction dominates the pressure profile.

The observed behaviour is as one would expect: reducing the surface charge density reduces the electrostatic repulsion between plates (Fig. 5.8). However, we notice that the structure of the pressure profiles and the location of the "wiggle" is different when electrostatic coupling is accounted for, and the difference is more marked the greater the value of $\sigma$. With the understanding gathered from the previous chapter, this is also to be expected: the higher the surface charge density, the greater the energetic cost of keeping a dielectric in a nonuniform field. This is shown in Fig. 5.8 from which it is evident that expulsion starts at larger values
CHAPTER 5. MODEL II: DIELECTRIC POLYMERS

Figure 5.7: Net osmotic pressure as a function of plate separation $H \equiv D/\lambda$ for different surface charge densities $\sigma$, as labelled (other parameters as in Table 5.1). Coupled (solid lines) and uncoupled (dotted) solutions are shown.
of $H$ the higher the value of $\sigma$ (while, clearly, the uncoupled prediction for the polymer contribution is independent of $\sigma$).

![Figure 5.8: Electrostatic ($>0$) and polymer ($<0$) contributions to the net osmotic pressure as a function of plate separation $H \equiv D/\lambda$ for different surface charge densities, $\sigma$. Coupled (solid lines) and uncoupled (dotted) solutions are shown.](image)

In addition to this effect, we notice in the coupling case, before the expulsion has occurred, a slight reduction to the ion contribution to the osmotic pressure. This is what we found in Chapter 4: the dielectric molecules lower the permittivity of the solution decreasing the electrostatic repulsion. The two coupling effects act in a direction that makes the pressure profile less repulsive. However, the effect of such changes is somewhat diluted by the fact that an increased electrostatic repulsion is necessary to bring them about in the first place.

**Effect of Reservoir Salt Concentration**

The effect of changing the salt concentration in the reservoir, $c_s^*$, is shown in Fig. 5.9.

We see that an increase in $c_s^*$ has a similar effect to the decrease in $\sigma$ of Fig.
CHAPTER 5. MODEL II: DIELECTRIC POLYMERS

Figure 5.9: Net osmotic pressure as a function of plate separation $D(\text{Å})$ for different reservoir surface salt concentrations $c_s^r$, as labelled (other parameters as in Table 5.1). Coupled (solid lines) and uncoupled (dotted) solutions are shown.
5.5. RESULTS

5.7. This is a trivial consequence of the greater screening of the electrostatic interactions as more salt is added to the reservoir. Fig. 5.10A displays how the electrostatic contribution to the pressure becomes negligible beyond a separation which is smaller, the larger the value $c_s^r$.

The difference between coupled and uncoupled cases, upon variation of the salt concentration, seems to have roughly the same effect for all concentrations in the range studied.

Fig. 5.10A sheds light on the dielectric reduction in pressure caused by the coupling. Notice the reduction is less pronounced, the larger the value $c_s^r$. This is the same trend observed in Section 4.5.4. We can ascribe it to the fact that a more efficient screening of the field (a sharper field gradient) entails a more efficient the expulsion of dielectrics which, in turn, raises the permittivity of the intraplate medium closer to that considered by the uncoupled approximation (where the permittivity is that of the solvent). Such differences in expulsion are evidenced if the separation by the corresponding screening length $\lambda$, as shown in Fig. 5.10B. We see that, for each profile, the expulsion happens for larger $H$ with respect to the uncoupled case, the larger the value $c_s^r$ (i.e., the smaller the value of $\lambda$).

However, the "absolute" difference between coupled and uncoupled polymer contributions to the osmotic pressure doesn't appear to be greatly affected by a change in $c_s^r$, with the expulsion being only slightly anticipated by a decrease in $c_s^r$ (Fig. 5.10C). This decrease is the opposite trend as observed in the rescaled case, and is due to the fact that although a more screened field will expel more efficiently, the field strength (on which the expulsion also depends) at a given separation is larger the smaller the screening length.

A variation of $c_s^r$ clearly has no influence on the uncoupled polymer contribution, and, once the separation is "scaled up" to Å, the results for all salt concentrations collapse onto the same line (as shown for two cases in Fig. 5.10C).

The weak dependence of the polymer contribution explains why the wiggle does
not travel significantly as $c_τ$ is reduced, in contrast to the effect of a variation of $σ$ at fixed $c_τ$. However, as we shall soon see in following sections, the expulsion can be made to happen at large separations by changing the range of the polymer attraction ($\sim$ the solution correlation length), in which case the reduction of the repulsion and the increased attraction for low $c_τ$ will cause more significant changes (see Section 7.2.2 of Chapter 7).

Figure 5.10: Electrostatic ($>0$) and polymer ($<0$) contributions to the net pressure as a function of plate separation $D(\lambda)$ (A,C) and rescaled separation $D/\lambda$ (B). Coupled (solid lines) and uncoupled (dotted line or empty circles) solutions are shown.
5.5. RESULTS

Polymer Parameters

Effect of $\chi$ parameter

In Fig. 5.11 we show the effect of changing the polymer solution's $\chi$ parameter. The overall magnitude of the pressure is seen to fall with increasing $\chi$, as the position of the pressure wiggle moves to higher values of the normalised separation $H$.

![Graph showing net osmotic pressure as a function of plate separation $H \equiv D/\lambda$ for different values of the $\chi$ parameter, as labelled (other parameters as in Table 5.1). Coupled (solid lines) and uncoupled (dotted) solutions are shown.](image)

Figure 5.11: Net osmotic pressure as a function of plate separation $H \equiv D/\lambda$ for different values of the $\chi$ parameter, as labelled (other parameters as in Table 5.1). Coupled (solid lines) and uncoupled (dotted) solutions are shown.

For the uncoupled situation we can explain these occurrences: increasing the $\chi$ parameter towards its theta value ($\chi = 0.5$) increases the range of the correlation between monomers (in a pure solution this changes the scaling of the correlation length), increasing the separation at which depletion effects cause an attractive contribution to the pressure (Fig. 5.12).
Figure 5.12: Electrostatic (＞0) and polymer (＜0) contributions to the osmotic pressure as a function of plate separation \( H \equiv D/\lambda \) for different values of the \( \chi \) parameter. Coupled (solid lines) and uncoupled (dotted) solutions are shown.

The reduction in the overall magnitude of the osmotic pressure thus results from the shorter range at which the polymer attraction kicks in (as a result of increasing \( \chi \)) and not from an increase in the magnitude of the polymeric (attractive) contribution to the osmotic pressure (which, in fact, decreases with increasing \( \chi \)).

From Fig. 5.12 we can also see how the coupling makes the expulsion happen at slightly larger values of \( H \), the difference being more pronounced as \( \chi \) increases. We can account for this roughly by considering that the greater extent of the polymer correlations allows electrostatic effects to propagate further (without being screened out by polymer).

The previously mentioned "dielectric" reduction of the ion pressure (shown only for \( \chi = 0.495 \) and the uncoupled case) contributes less significantly to the different predictions. Its contribution is more important, the greater the value of \( \chi \), since the correlation between monomers are greater and the penalties associated with keeping low permittivity dielectrics in a nonuniform field more easily felt.
5.5. RESULTS

Clearly, changing $\chi$ has no effect on the ionic contribution to the pressure when coupling is not accounted for.

**Effect of Reservoir Polymer Concentration**

Next in our parameter study we look at the effect of varying the reservoir monomer concentration, $\phi^r$, which in Chapter 7 we will use to control the total polymer content of a lamellar phase in contact with a salt bag.

Observe that decreasing $\phi^r$ produces a broadly similar effect to increasing $\chi$: the pressure becomes less repulsive and the wiggle moves pronouncedly to larger $H$.

![Figure 5.13: Net osmotic pressure as a function of plate separation $H \equiv D/\lambda$ for different reservoir monomer volume fractions $\phi^r$, as labelled (other parameters as in Table 5.1). Coupled (solid lines) and uncoupled (dotted) solutions are shown.](image)

Again, in the uncoupled situation we can explain this behaviour by an increase in the correlations between monomers with decreasing volume fraction and the
osmotic pressure is overall reduced because of a range effect, not because of an increasing value of the polymer reservoir pressure, which decreases with decreasing monomer concentration, as one would expect.

The differences between uncoupled and coupled behaviour are accountable mainly to electrostatic depletion whose effect increases with decreasing $\phi^r$ (Fig. 5.14). This trend is a result, as for $\chi$, of the increased correlation length of the polymer solution, which allows the electrical influence on the dielectric polymers to propagate further and call for an earlier expulsion.

The "dielectric" reduction of the ion pressure (shown only for $\phi^r = 0.25$ and the uncoupled case) contributes less significantly to the different predictions. Its contribution is more important, the greater the value of $\phi^r$: there's more polymer between the plates and it is expelled "later", since the correlation to the walls has diminished.

![Graph](image.png)

Figure 5.14: Electrostatic ($>0$) and polymer ($<0$) contributions to the osmotic pressure as a function of plate separation $H = D/\lambda$ for different values of $\phi^r$. Coupled (solid lines) and uncoupled (dotted) solutions are shown.
Clearly, changing $\chi$ has no effect on the ionic contribution to the pressure when coupling is not accounted for.

**Effect of Reservoir Polymer Concentration**

Next in our parameter study we look at the effect of varying the reservoir monomer concentration, $\phi^r$, which in Chapter 7 we will use to control the total polymer content of a lamellar phase in contact with a salt bag.

Observe that decreasing $\phi^r$ produces a broadly similar effect to increasing $\chi$: the pressure becomes less repulsive and the wiggle moves pronoucnedly to larger $H$.

![Graph](image)

**Figure 5.13:** Net osmotic pressure as a function of plate separation $H \equiv D/\lambda$ for different reservoir monomer volume fractions $\phi^r$, as labelled (other parameters as in Table 5.1). Coupled (solid lines) and uncoupled (dotted) solutions are shown.

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![Figure 5.14](image_url)

Figure 5.14: Electrostatic ($> 0$) and polymer ($< 0$) contributions to the osmotic pressure as a function of plate separation $H \equiv D/\lambda$ for different values of $\phi^r$. Coupled (solid lines) and uncoupled (dotted) solutions are shown.
5.5. RESULTS

Dielectric Parameters

In this final section we look at the parameters which determine the extent of the electrostatic coupling between the polymers and the charged surfaces: the dielectric contrast between the polymer and the surrounding solvent, and the size of the dielectric unit associated with each lattice monomer. The uncoupled limit can be thought of as resulting from a gradual vanishing of these parameters. For example, "permittivity matching" the polymer and solvent would make the polymer electrostatically invisible to the surface, removing all coupling effects.

Effect of Dielectric Contrast

Shown in Fig. 5.15 is the effect of decreasing the dielectric contrast from from \( \approx 40 \) to 1 by changing the polymer permittivity from that of oil, \( \varepsilon_2 = 2 \), to that of water, \( \varepsilon_2 = 78.5 \).

As expected, the difference between coupled and uncoupled predictions for \( \Pi \) is reduced as the dielectric contrast is diminished. The difference is greatest for "oily" solutes, but is still pronounced for a polymer with \( \varepsilon_2 = 25 \), roughly the permittivity of ethanol. The agreement between the coupled case in the absence of contrast (\( \varepsilon_2 = 78.5 = \varepsilon_1 \)) and the uncoupled case provides a useful check on the coupled solutions.

Fig. 5.16 shows the contributions to the osmotic pressure. We observe the expected trends: the electrostatic repulsion is reduced for larger values of contrast, as predicted by Model I; the expulsion is anticipated. The first is the effect of the polymer on the electrostatics: before expulsion, the permittivity between the plates is decreased in a manner which is greater, the bigger the dielectric contrast. After expulsion, the contribution matches the uncoupled one, with a change of slope, as noticed earlier. The expulsion results, as usual, from the electrostatic penalty of keeping dielectrics in a nonuniform field. The penalty is greater, the
Figure 5.15: Net osmotic pressure as a function of plate separation $H \equiv D/\lambda$ for different values of the polymer permittivity $\varepsilon_2$, (other parameters as in Table 5.1).
5.5. RESULTS

greater the dielectric contrast, which explains the observed trends for the polymer expulsion.

Figure 5.16: Electrostatic (> 0) and polymer (< 0) contributions to the net osmotic pressure as a function of plate separation $H = D/\lambda$ for different values of the polymer permittivity $\varepsilon_2$.

**Effect of Dielectric Size ($f$ factor)**

Finally, we have changed the factor $f$, which determines how much smaller a dielectric unit is than the polymer lattice length it is associated with. Recall from Section 5.1.1 that $f$ is a measure of the volume of polarisable matter in a polymer.

Fig. 5.17 shows that when $f$ is reduced from 2 (dielectric diameter $=$ lattice length) to 1.1 (dielectric radius $\simeq$ lattice length) the net osmotic pressure is considerably reduced in magnitude and the wiggle is moved to higher values of $H$.

As before, Fig. 5.18A displays the contributions to the pressure. Analogously to the effect of dielectric contrast, decreasing $f$ (increasing the dielectric volume)
Figure 5.17: Net osmotic pressure as a function of plate separation $H \equiv D/\lambda$ for different values of the dielectric size factor $f$. The parameters used are those of table Table 5.1, except for $\chi$, which is as labelled.
5.6. SUMMARY AND CONCLUDING COMMENTS

at the values shown, reduces the repulsion and anticipates the expulsion. The coupling effects prove dramatic for $f = 1.1$. We see a noticeably anticipated expulsion and a sharp reduction in the repulsion before expulsion is complete and the pressure is restored to the uncoupled limit. Such strong coupling evidences the transition from an electrostatic repulsion in a medium with the permittivity of a polymer solution permittivity to that of medium with the permittivity of the solvent. This "bend" in the repulsive pressure is shown in Fig. 5.18 on a log-scale to evidence the change of slope between the two limits.

5.6 Summary and Concluding Comments

In this chapter we have developed Model II from Model I to describe the interaction between charged plates immersed in an ionic polymer solution.

With the inclusion of non-ideal terms in the dielectric free energy, the model now accounts for the cost of restricting the polymer to energetically unfavourable regions between the plates. Signs of this are evident in the example solutions presented, where we see the polymer concentration decreasing close to the surfaces. This depletion can be sufficiently high as to make the polymer leave the space between the plates completely. Such a polymer vacuum causes the plates to attract each other, yielding an osmotic interaction profile very different from the monotonic repulsion of Chapter 4. The presence of the dielectric, similarly to Model I, provides an additional source of screening for the electrostatic potential. If the polymer is not expelled from between the surfaces the latter effect causes a reduction in the repulsive (electrostatic) contribution to the pressure. On the other hand, polymer expulsion restores the repulsive contribution of the pressure to its original value. This effect is most dramatic for large coupling between the polymer and the surfaces.

The osmotic pressure is sensitive to parameter variation in a way which reflects the effect of the parameters on the electrostatics, on the polymer physics and
Figure 5.18: (A) Electrostatic (> 0) and polymer (< 0) contributions to the net osmotic pressure as a function of plate separation $H = D/\lambda$, for different values of the dielectric size factor $f$. (B) Logarithmic plot of the pressure to highlight the bend in the repulsive contribution for $f = 1.1$ which is discussed in the text.
on how they couple. In the absence of coupling, we can crudely describe the behaviour in terms of the range and strength of the polymer and electrostatic interaction. The latter has a strength which increases with increasing surface charge density and is screened in a manner proportional to the salt concentration in the reservoir. The polymer attraction has a strength which depends on the reservoir monomer concentration and a range which depends on the correlations between monomers. This decreases with increasing polymer concentration and as the $\chi$ parameter is decreased away from 1/2.

Coupling complicates matters, and such a crude description, in general, is no longer valid. The effect of coupling manifests itself through an enhanced polymer depletion (as expected from Model I) and a reduced electrostatic repulsion (as observed in Model I). The “electrostatically assisted” depletion and the reduced repulsion have the same electrostatic dependencies as in Model I (see Section 4.5.4), with the exception of salt concentration, for the reasons explained in Section 5.5.5. In addition, because the effects of the field on the dielectric monomers can propagate further when monomers correlate more efficiently, electrostatically assisted expulsion and repulsion reduction are enhanced for $\chi$ parameters close to 1/2; for the same reason expulsion is favoured at low reservoir monomer concentrations, $\phi^r$. The reduced repulsion on the other hand, is biggest at higher values of $\phi^r$, since the dielectric screening is greater for greater concentrations of dielectric.

Our results on the effect of coupling highlight the nonadditivity of polymeric and electrostatic contributions to the osmotic pressure between charged surfaces in the presence of dielectric contrast. Such nonadditivity is often ignored in theoretical descriptions of systems (e.g. doped lamellar phases), whose dielectric make-up begs its inclusion (at least to demonstrate the reasons why additivity is a good approximation for most realistic systems). We will discuss these matters in more detail in chapters 7 and 8.

Finally, we would like to point out the resemblance of the osmotic pressure to
a Van der Waals isotherm, with its unphysical \( S \) shape. By analogy with a fluid system, this suggests the possibility of phase separation. But what is phase separating? The next chapter is devoted to mapping the present model onto lamellar phases doped with polymers. We shall see what the phase separation means in this context, and how the present model can be adapted to construct phase diagrams to predict the behaviour of these interesting mixtures.
Chapter 6

Mapping Model II onto Smectics

In this chapter we adapt Model II of Chapter 5 to provide an approximate description of aqueous lamellar phases whose water layers are doped with non-adsorbing polymer. Our final goal is to make qualitative predictions as to the phase behaviour of such systems, presented in Chapter 7, which we hope be experimentally detectable in systems similar to those described in Chapter 3.

After geometrically and thermodynamically mapping Model II onto lamellar stacks, we will describe how the phase equilibria of “model smectics” can be extracted from the solution of its equations.

6.1 Geometrical Relations

At the end of Chapter 5 we applied Model II to the simple case of a solution (water+solutes) slab delimited by parallel surfaces of infinite extent. We saw in Section 3.1 that lamellar phases consist of a periodic succession of fluctuating surfactant bilayers. If we neglect the fluctuations of the layers and assume their lateral extension is not relevant to their phase behaviour, a charged lamellar phase is simply a succession of alternating solvent and bilayer slabs, the geometry of the solvent slab, parallel surfaces, being identical to that described by Model II.
We will consequently approximate doped lamellar phases as a succession of repeating units, each comprising a solution filled slab, of thickness $D$, and a bilayer filled slab, of thickness $\delta$. The period (repeat distance) of the lamellar phase is thus $D + \delta$. Fig. 6.1 shows this relation and how the previous model maps onto lamellar phases:

![Diagram](image)

Figure 6.1: How a lamellar phase can be approximated by a succession of units, each comprising charged parallel planes separated by $D$ (described by Model II) and a layer of thickness $\delta$. The periodicity of the lamellar phase is $D + \delta$.

**Bilayer Volume Fraction**

In experiments, phase diagrams are constructed from information about the surfactant and polymer content of a doped lamellar system (see e.g. Fig. 3.1). Above the CMC, the surfactants in the system reside, to a very good approximation, almost entirely in the bilayers. The volume fraction of bilayers\(^1\) is thus identical to the surfactant volume fraction.

\(^1\)"Membrane volume fraction" is also used [85].
As we shall see, our model allows us to predict the lamellar spacings $D$ at which phases coexist, so we need to convert this information into the experimentally accessible volume fraction information. This is easily derived. Let $N_b$ be the total number of lamellar bilayers, $v_b = A\delta$ be the volume of a bilayer of area $A$ and $v_s = AD$ the volume of a solvent layer of the same extent. Then, since the total volume of the lamellar phase is $V = N_b(v_s + v_b)$, the bilayer volume fraction, defined as $\phi_b = N_b v_b / V$, is:

$$\phi_b = \frac{v_b}{v_s + v_b} = \frac{\delta}{D + \delta} \quad (6.1)$$

We have derived the quite obvious statement that the volume fraction of a rigid lamellar phase is given by the bilayer thickness divided by the periodicity of the phase. Equation (6.1) is known as the classical swelling law of a lamellar phase. An expression for the polymer content of the lamellar phase will be derived in section Section 6.3.3.

### 6.2 Thermodynamics

Next we develop the thermodynamic relations that describe a lamellar stack and find their relation to Model II.

For the mapping between models to be the simplest possible we imagine the lamellar stack to be in contact with same reservoir of ions and polymer which contacted the parallel surface system of Chapter 5. The contact is through a membrane which doesn't let the bilayers through, so that the bilayer content of the phase is fixed (recall we assume the surfactants only reside in the membrane and are virtually insoluble in the solvent). In this way a lamellar phase is thermodynamically equivalent to a series of $N_b$ such systems each in equilibrium with the reservoir and, consequently, each other Fig. 6.2A,B.
The lamellar phase is described in a semi-grand ensemble: it has a fixed bilayer composition and a variable polymer and ionic content. We shall denote the relevant thermodynamic potential by $\Xi = \Xi(N_b, T, V, \mu_j)$, where the dependencies indicate the thermodynamic variables which minimise $\Xi$ at equilibrium: temperature $T$, volume $V$, number of bilayers $N_b$, and chemical potential $\mu_j$ for species $j$ ($j = \text{ions or polymer}$).

6.2.1 Relation Between Thermodynamic Potentials

As mentioned, the bilayers are assumed rigid and the surfactants they are made of are approximated as insoluble in water. Here we further assume that all non-electrostatic interactions associated with the bilayer (e.g. dispersion attraction between bilayers) can be ignored. These assumptions entail that the bilayers contribute nothing to the free energy of the assembly (or rather, they contribute only a constant self-energy of formation to which we can shift the energetic zero). The only contributions to the free energy originate in the solvent layers. Since
energy is an extensive thermodynamic variable and pressure intensive, we can immediately determine the stack semi-grand potential, \( \Xi \), and its pressure, \( \Pi_{\text{lam}} \). (Henceforth \( \Pi_{\text{lam}} \) will indicate the osmotic pressure between the lamellar phase and the reservoir, through the semipermeable membrane: \( \Pi_{\text{lam}} = p_{\text{lam}} - p_{\text{res}}, \) where \( p_{\text{res}} \) is the reservoir pressure). They are given by:

\[
\Xi = N_s \Omega_s \\
\Pi_{\text{lam}} = \Pi_s
\]

(6.2)

(6.3)

Where \( \Omega_s \) and \( \Pi_s \) are respectively the grand potential and the osmotic pressure of the solvent slabs (\( \Pi_s \) is equivalent to \( \Pi_{\text{net}} \) used in Chapter 5). We thus have everything we need to describe lamellar phase equilibria, except for an explicit expression for the chemical potential associated with the change in the number of bilayers (slabs) upon phase separation. We will call the latter "bilayer chemical potential" and denote it by \( \mu_b \), since it will determine the volume fraction of bilayers in each coexisting region of a phase separated lamellar stack.

### 6.2.2 Lamellar Thermodynamic Variables from \( \Xi \)

We present below a general derivation of the thermodynamic variables of interest; as mentioned, we are only missing the chemical potential, so this is partly redundant. However, this particular approach makes the relations to the previous description of the parallel surface system particularly clear.

Recall \( \Xi \) is a semi-grand potential, thermodynamically defined as \( \Xi = E - TS - \sum_j \mu_j N_j \) (where the "semi" comes from the exclusion of the bilayers as a species in the subtracted summation), where \( E \) is the internal energy of the lamellar system and \( S \) is its entropy. The first law in differential form for the lamellar stack reads

\[
dE = TdS - \Pi dV + \sum_j \mu_j dN_j + \mu_b dN_b,
\]

where \( \mu_b \) is the bilayer chemical potential.

This is also "osmotic" with respect to the pure solvent.
Using this and the definition of $\Xi$ we can thus write the following differential for $\Xi$:

$$d\Xi = SdT - \Pi_{lam}dV + \mu_b dN_b - \sum_j N_j d\mu_j$$  \hspace{1cm} (6.4)

And, since $\Xi = \Xi(N_b, T, V, \mu_j)$, we also have:

$$d\Xi = \left( \frac{\partial \Xi}{\partial N_b} \right)_{T,V,\mu_j} dN_b + \left( \frac{\partial \Xi}{\partial T} \right)_{N_b,V,\mu_j} dT + \left( \frac{\partial \Xi}{\partial V} \right)_{N_b,T,\mu_j} dV + \sum_j \left( \frac{\partial \Xi}{\partial \mu_j} \right)_{N_b,V,T} d\mu_j$$  \hspace{1cm} (6.5)

Comparing (6.4) and (6.5), we see that the stack pressure $\Pi_{lam}$ and bilayer chemical potential $\mu_b$ are given by:

$$\Pi_{lam} = - \left( \frac{\partial \Xi}{\partial V} \right)_{N_b,T,\mu_j}$$  \hspace{1cm} (6.6)

$$\mu_b = \left( \frac{\partial \Xi}{\partial N_b} \right)_{T,V,\mu_j}$$  \hspace{1cm} (6.7)

It is also useful to express the semi-grand potential $\Xi$ as an intensive quantity, since we will show in Section 6.3.2 that this allows a geometrical interpretations of the conditions for phase equilibrium. Dividing $\Xi$ by the lamellar volume, we define the free energy density:

$$f_\Xi = \frac{\Xi}{V} = \frac{\Omega}{D + \delta}$$  \hspace{1cm} (6.8)

where we have used $V = N_b(D + \delta)$. Thus, substituting $\Xi = f_\Xi V$ into Equations (6.6) and (6.7), yield expressions for $\Pi$ and $\mu_b$ in terms of $f_\Xi$:

$$\Pi_{lam} = - f_\Xi + \phi_b \left( \frac{\partial f_\Xi}{\partial \phi_b} \right)_{N_b,T,\mu_j}$$  \hspace{1cm} (6.9)

$$\frac{\mu_b}{\delta} = \left( \frac{\partial f_\Xi}{\partial \phi_b} \right)_{T,V,\mu_j}$$  \hspace{1cm} (6.10)
6.2.3 Lamellar \( \Pi \) and \( \mu_b \) from Model II

Recall the thermodynamic potential of the solvent slab, described by Model II, is \( \Omega_s = \Omega(T, v_s, \mu_j) \), in the notation of this chapter. Equation (6.2) relates the two potentials, so that we can use it together with (6.6) and (6.7) to express \( \Pi \) and \( \mu_b \) as derivatives of \( \Omega_s \). However, when doing this, we need to carefully account for the dependencies of \( \Omega_s \). With the latter explicitly written out, Equation (6.2) reads:

\[
\Xi(N_b, T, V, \mu_j) = N_b \Omega(T, v_s, \mu_j)
\]

\[
\Xi(N_b, T, V, \mu_j) = N_b \Omega \left( T, \frac{V}{N_b} - v_b, \mu_j \right)
\]

where we have used the fact that the total volume of the stack is \( V = N_b(v_b + v_s) \). Thus, from Equation (6.6) the osmotic pressure is found to be identical to the net pressure exerted by one solvent layer on its surface (the pressure of the Model II):

\[
\Pi_{\text{lam}} = -\left( \frac{\partial \Xi}{\partial V} \right)_{N_b} = N_b \frac{1}{N_b} \left( \frac{d\Omega}{dv_s} \right) \equiv \Pi_s \tag{6.11}
\]

The chemical potential, in turn, is found from (6.7) to be:

\[
\mu_b = \left( \frac{\partial \Xi}{\partial N_b} \right)_V = \Omega + N_b \left( \frac{d\Omega}{dN_b} \right)_V \tag{6.13}
\]

To relate this expression to the Model II, consider the meaning of \( (d\Omega/dN_b)_V \): it is the change of the energy of one solvent slab with the number of bilayers, as the total stack volume is held fixed. If we imagine adding one bilayer to a lamellar
phase of fixed volume, the solvent slab spacing has to change by a bilayer width to conserve the total volume. An amount of work \( dW = \Pi_{lam} dv_s \) needs to be done against the osmotic pressure of the stack to accommodate the new layer, the energy of the stack is thus increased by the negative of this work: \( d\Omega = -\Pi_{lam} dv_s \). Equation (6.13) thus becomes:

\[
\mu_b = \Omega - N_b \Pi_{lam} \left( \frac{dv_s}{dN_b} \right)_V
\]  

(6.14)

and since \( (dv_s/dN_b)_V = -V/N_b^2 \) \( (v_s = V/N_b - v_b) \), we obtain:\n
\[
\mu_b = \Omega + \Pi_{lam}(v_s + v_b)
\]  

(6.15)

We can calculate \( \Pi_{lam} = \Pi_s \) from Model II. To find \( \Omega \), Equation (6.12) allows to write \( \Omega = -\int \Pi_{lam} dv_s + const \), since the energy is defined up to a constant. Equation (6.15) then becomes an equation in \( \Pi_{lam} \) only:

\[
\mu_b = -\int \Pi_{lam} dv_s + \Pi_{lam}(v_s + v_b) + const
\]  

(6.16)

In the limit of an infinitely swollen lamellar phase \( (D \to \infty) \), the solvent slab and the reservoir coincide, so that \( \Pi_{lam}(D \to \infty) = 0 \) (remember the pressure is defined with respect to the reservoir). Considering this and rewriting (6.16) with \( v_s = AD \) and \( v_b = A\delta \), we can redefine the chemical potential as:

\[
\frac{\mu_b}{A} = \mu_b(D) - \mu_b(D \to \infty) = \Pi_{lam}(D + \delta) - \int_{\infty}^{D} \Pi_{lam} dD
\]  

(6.17)

\[\text{Equation (6.15) could have been derived a lot more quickly as follows:} \]

\[\mu_b \equiv G/N_b = (\Xi + \Pi_{lam} V)/N_b = \Omega + \Pi_{lam}(v_s + v_b). \] Where we have used the fact that the bilayer chemical potential is \( G \), the Gibbs free energy per bilayer.
6.3 Phase Coexistence

With the relationships we have just derived it is possible to obtain predictions for the equilibria of doped lamellar phases. What do we expect these equilibria to be? We saw at the end of Chapter 5 how the force between charged surfaces in a reservoir has effective attractive and repulsive contributions to the pressure, as a result of the competition between energetic and entropic tendencies of the ions and polymers in solution. A uniform lamellar phase has the option of lowering its energy by rearranging its bilayers to maximise the entropy of the polymer solution and minimise the electrostatic repulsion between bilayers: one possible phase equilibrium is the coexistence between two lamellar phases of different spacings, one large, to reduce the electrostatic repulsion, and one small, to make more space for the polymer in the large one. The situation is analogous to the liquid–gas coexistence of simple liquids, an analogy which shows in the similarity of the results of a mean field description: the shape of the osmotic pressure displays the same undulation as the Van der Waals prediction for a gas, as observed in Section 5.6. A limiting case of the Lamellar–Lamellar (LαLα) coexistence arises when the electrostatic repulsion is so weak that the coexisting phase of large spacing is identical with the reservoir: the reservoir coexists with the smectic phase (LαL coexistence).

Recall from Chapter 3 that these qualitative expectations are indeed fulfilled in the experimental observations of polymer doped lamellar phases.

6.3.1 Ensembles

Our models so far have assumed a polymer and ion reservoir to contact the system, mostly for calculational convenience. Experimentally, however, it is most convenient to specify the relative amounts of the constituent components that are mixed in a solution. By construction, canonical (experimental) or grand canonical
formulations (our model) predict the same thermodynamic variables, and from these, the same equilibria follow.

For comparison with experiment, we need to specify the composition of coexisting phases. In theory these follow by differentiation of $\Xi$, like the other thermodynamic variables of the problem. For practical reasons, however, it has proved more convenient to evaluate the content of coexisting phases by integration of the density profiles predicted by Model II, as we will see in Section 6.3.3.

### 6.3.2 Phase Equilibria from Model II

For two thermal systems 1 and 2 to be in equilibrium, we require a thermal, mechanical and chemical balance between them. The reservoir is a heat bath, making the lamellar phase is isothermal and the condition of equal temperatures redundant. Thus, the equilibrium conditions are, in our case:

\[
\Pi_{lam}^1 = \Pi_{lam}^2 \tag{6.18}
\]

\[
\mu_b^1 = \mu_b^2 \tag{6.19}
\]

Equation (6.18) expresses the osmotic balance between the phases, while Equation (6.19) expresses the balance of the two phases with respect to bilayer exchange. In the special case of a phase of finite period coexisting with one of infinite separation, the above reduce to:

\[
\Pi_{lam} = 0 \tag{6.20}
\]

which expresses the osmotic balance between the reservoir and the lamellar phase. Once more we have assumed the composite system to be isothermal. Note also that we didn’t include a chemical potential balance in this case. As will become evident from the geometrical interpretation of equilibria just below, the inclusion
of chemical potential equality is not necessary because the chemical potential of the coexisting "reservoir phase" is null.

**Common Tangent Construction**

One possible geometrical interpretation of the equilibrium conditions, known as *common tangent construction*, is possible using the relations derived in Section 6.2.2. Fig. 6.3A displays a plot the semi-grand potential per unit volume, $f_\Xi$, against bilayer volume fraction. As shall see, the tangent to $f_\Xi$ indicates lamellar–lamellar coexistence.

![Common Tangent Construction Diagram](image)

Figure 6.3: The equivalent common tangent construction (A) and equal area (B) geometrical constructions discussed in the text can be used to predict coexisting lamellar phases from a mean field theory. Starred quantities indicate equilibrium values.

Note that $f_\Xi$ displays an undulation. This is a consequence of the fact that we are using a mean field model, which does not include phase separation as a means of reducing the system energy. It is possible to "correct" this omission using the
common tangent construction: a line is drawn, as shown in Fig. 6.3A, tangent to $f_E(\phi_b)$ at the two points shown. Phase separation into two coexisting lamellar phases 1 and 2, corresponding to the drawing of this line, lowers the free energy and frees it of the unphysical convexity in the coexistence region.

The tangent through 1 and 2 is: $f^2_2 - f^2_1 = m(\phi^2_b - \phi^1_b) + p$, where $m$ and $p$ are the line's gradient and intercept respectively. Using Equations (6.9) and (6.10) we can also write: $f^2_2 - f^1_2 = \mu_b/(A\delta)(\phi^2_b - \phi^1_b) - \Pi$; it is thus possible to identify $m = \mu_b/(A\delta)$ and $p = -\Pi$. The common tangent's slope is the chemical potential of the bilayer (up to a constant) and its intercept with the y-axis is the negative of the osmotic pressure. The region between 1 and 2 is then a region of constant pressure and chemical potential: 1 and 2 are coexisting lamellar phases with volume fractions $\phi^1_b$ and $\phi^2_b$ respectively.

The common tangent construction is a graphical method of finding phase equilibria, which would otherwise have to be obtained from the solutions of (6.18) and (6.19).

In the case of coexistence between the lamellar phase and a "lamellar–less" reservoir the common tangent construction needs to be treated with care [74]. The appropriate construction on $f_E$ is shown in Fig. 6.4A.

Once more it is possible to lower the free energy, but this time a "virtual tangent" connects $f_E$ and the origin, where the state of the reservoir is collapsed (its pressure and chemical potential are null). The reason for the absence of an ordinary common tangent is due to the approximation which constrains the surfactants to reside only in the bilayer. In reality, an exponentially small fraction of surfactants will be able to diffuse into the reservoir and coexist with the bilayers (see inset of Fig. 6.4A).
6.3. PHASE COEXISTENCE

Figure 6.4: The special case of virtual tangency (A) and the equivalent “trivial” equal area construction (B). The constructions allow to establish the coexistence between a a lamellar phase of finite separation and a reservoir, assumed “bilayer–less”. The latter assumption means we can consider the point \((0,0)\) in (A) or \((0,\infty)\) in (B) to be a coexisting “reference” state. This lifts any constraint on the chemical potential, but in reality an exponentially small amount of surfactants coexisting with the lamellar phase resides in the reservoir, as shown in the inset of (A).
Equal Area Construction

The common tangent construction is a useful tool for visualising equilibrium and can be used to establish the coexisting lamellar volume fractions. However, for practical reasons, we found it more convenient to use an equivalent geometrical method. This method, the Maxwell equal area construction, only requires a knowledge of the osmotic pressure, a quantity which stems directly from our model (as we have seen, \( \Omega \) is obtained from it by integration).

It is instructive to show how this construction is equivalent to the conditions for equilibrium (and so to the common tangent construction). Let \( D_1 \) be the spacing between solvent layers in phase 1 and \( D_2 \) that in phase 2. Then, using Equation (6.17), we can re-write (6.18) and (6.19) as:

\[
| r_1 - \gamma = \gamma_{\text{lam}} \]

\[
\frac{\mu_1^b}{A} - \frac{\mu_2^b}{A} = \Pi_{\text{lam}}^* (D_1 - D_2) + \int_{D_1}^{D_2} \Pi_{\text{lam}}^* dD = 0 \quad (6.22)
\]

Condition (6.22) is a mathematical statement of the Maxwell equal area construction\(^{iv}\), shown in Fig. 6.3B. The construction involves drawing a horizontal line at the value of the pressure which equalises the areas defined by the wiggle in the pressure. As shown above the construction amounts to determining the pressure at which the separated phases, which lower the free energy, coexist. We thus have a recipe for finding coexisting phases from the net osmotic pressure as found in the Model II: the equilibrium osmotic pressure \( \Pi_{\text{lam}}^* \) is the one which satisfies the equal area criterion, and the solvent spacings at which the two lamellar phases coexist are the innermost and outermost distances that exist at this pressure.

The construction is trivial for the lamellar–reservoir coexistence: the coexistence separation is found where the osmotic pressure cuts the zero axis, as shown in

\(^{iv}\)Which could have been derived directly from the Gibbs–Duhem relation, as is done in most thermodynamics textbooks [29] or from the Clausius inequality applied to the reversible thermodynamic cycle 1234531 in Fig. 6.3 [101].
6.3.3 Polymer and Salt Content of Coexisting Phases

Now that a method for establishing phase equilibria from Model II has been formulated, it is convenient to extract the polymer and salt content of a phase. In Section 5.5.4 we showed how Model II allows to predict polymer and ion density profiles between charged surfaces. The total amount of a given species, is found by simple integration of these profiles. The total volume fraction of polymer is the fraction of the volume of the lamellar phase occupied by polymer, or since the lamellar phase is a succession of repeated units of volume \( v_3 + V_b \), it is the fraction of a unit occupied by polymer:

\[
\phi_p = \frac{v_p}{v_s + v_b}
\]

(6.23)

where \( v_p = A \int_0^D \phi_p(x)dx \): the volume \( v_p \) occupied by the polymer is found by the weighing each volume element \( dv = Adx \) by the polymer volume fraction profile \( \phi(x) \). We therefore can write:

\[
\phi_p = \frac{1}{D + \delta} \int_0^D \phi_p(x)dx
\]

(6.24)

where, as usual, \( v_s = AD \) and \( v_b = A\delta \). Equation (6.24) gives the average polymer concentration of polymer in the solvent layers of a lamellar phase as a function of the solvent thickness. In particular we are now able to find what polymer concentrations correspond to the values of \( D \) (and so \( \phi_b \)) at which phases coexist (the polymer will partition between coexisting phases), as shown in Fig. 6.5.

In exactly the same way the salt content of a phase is found by integrating the positive ion concentrations. Recall the ion concentration is given by the Boltzmann factor \( n_i(x) = n_i^* e^{-eV(x)/T} \), so that defining the total salt concentration as \( n_s \equiv n_+/V \), we have:
Figure 6.5: Polymer and salt content of coexisting phases. Top to bottom: the Maxwell construction is applied on $\Pi$ to find $D_1$, $D_2$; intersecting the polymer concentration profile at these gives the polymer concentrations $\phi_p^1$, $\phi_p^2$ in each coexisting phase; and the salt concentrations $c_s^1$, $c_s^2$. 
6.4 Phase Diagram Prediction

Equation (6.25) is a recipe for finding the salt partitioning between coexisting phases (shown in Fig. 6.5). It is also a statement of the Donnan effect, as applied to the lamellar phase: since each lamellar phase is contacted with the reservoir through a membrane impermeable to the bilayers, salt is expelled from the lamellar phase.

Armed with Model II mapped onto lamellar phases, the Maxwell construction and relations (6.23)–(6.25), we have, in principle, all that is necessary for the construction of phase diagrams describing polymer doped charged smectics. The chemical potentials of the reservoir (as defined by the reservoir values polymer and electrolyte concentrations) can be used to systematically investigate the effect of polymer or salt content on the phase behaviour of our doped systems. However, since both these quantities are unconstrained in the determination of phase equilibria, our method does not allow for the determination of a completely canonical system. To make this clearer, let us make an example. Suppose we want to study the effect of adding polymer to a lamellar phase; to do this we change the chemical potential of the reservoir to progressively increase the polymer content of the phase and look for any resulting phase coexistences. We can thus plot the equilibrium bilayer concentrations and the corresponding polymer concentrations, but, unless the chemical potential of the ions has been adjusted to maintain the mean salt concentration, the coexisting phases will not add up to have the same salt content. Such adjustment of the salt chemical potential is awkward to implement, given the way we have set things up and, from now we will present results for a system which is “canonical” with the exception of the salt.
Here below we summarise the steps involved in the construction of a "canonical with the exception of the salt" phase diagram. Our objective is to study how polymer content affects the phase behaviour of a lamellar system when it is in contact with a salt reservoir. Experimentally we can imagine a container, in which we mix bilayers and polymers, which consists of a membrane sack immersed in a salt solution. The membrane has pores big enough to let ions through, but not polymers and bilayers. This kind of system is not so unrealistic: it is experimentally available and the membrane is known as a dialysis membrane\(^{v}\).

### 6.4.1 Phase Diagram Construction

The phase diagram we want to construct is a density-density phase diagram: polymer volume fraction, \(\phi_p\), versus bilayer volume fraction, \(\phi_b\). It is constructed as follows:

- we fix the electrostatic and polymer parameters of interest, except for the polymer reservoir concentration (chemical potential) of our model system, which is used as a control parameter to obtain corresponding pressure and actual polymer content profiles as a function of lamellar separation.

- the equal area construction is applied to the pressure to find the spacings of the coexisting lamellar phases. To the latter correspond the coexisting bilayer volume fractions by Equation (6.1).

- the polymer content of each of the coexisting phases is found by evaluating the polymer content profiles at the values of the equilibrium spacings (Fig. 6.5).

- the coordinates of coexisting phases we have found in this way can be plotted on the phase diagram as pairs of points: \((\phi_{b1}^1, \phi_p^1)\) \((\phi_{b2}^2, \phi_p^2)\).

\(^{v}\)The same kind of membrane was used by Thomas Graham in the 1860s when he distinguished molecular ("crystalloids") from colloidal ("colloids") matter.
• the coexisting phase points are joined by tie lines, which are oblique as there is not constraint for the volume fractions to be the same in a given phase.

The uncertainty in the position of the points on the phase diagrams derives from the method with which they have been obtained and, where this was very accurate, from the intrinsic accuracy of the numerics. The estimation of the magnitude of such uncertainties and the exact details of the phase diagram construction from Model II are left to Section A.6 of Appendix A.

**System with Fixed Salt and Polymer Content**

On a final note, we suggest how a phase diagram of the effect of polymer addition at fixed salt content could be obtained, rather laboriously: several phase diagrams could be found as above for many different values of the reservoir chemical potential (all other parameters being held fixed), evaluating the salt content of each phase point. It would then be possible to construct the corresponding phase diagrams for a fixed salt concentration. This proved not to be possible, however, with the time available for this thesis.
Chapter 7

Phase Behaviour of Polymer Doped Smectics

In this chapter we apply the theoretical description developed in Chapters 5 and 6.1 to the prediction of the phase behaviour of charged lamellar phases doped with a polymer solution.

Some of the experimental and theoretical literature on polymer doped charged smectics recognizes, or crudely accounts for, the possible influence of polymers on the electrostatic interaction between charged bilayers, through the reduction of the permittivity of the solution due to the polymer [76, 84, 102, 87]. However, to the best of our knowledge, no mention is made in the literature of the complementary influence of the electrostatics on the polymer physics\(^1\), which should be included in a realistic and consistent description of these systems.

The results presented in this chapter represent a study of the effects of the electrostatic coupling between polymers and charged bilayers, for experimentally reasonable conditions. First, with polymer properties held fixed, the effect of adding polymer to lamellar phases is studied for different bilayer charges and reservoir

\(^1\)Though, as mentioned in Section 5.2.2, Khokhlov et al. have included such effects in a mean field model of polyelectrolyte adsorption reported in [39].
ionic strengths. Then the sensitivity to polymer properties is studied. As we present the results, we shall try and explain them using the understanding developed in previous chapters.

The study that follows is carried out in the hope of shedding some light on situations, should they arise, where the electrostatic coupling between polymer and the bilayers cannot be ignored. To this end all results are compared with the prediction of a model which ignores the coupling, a neglect of which several of the models to be found in the literature are guilty, as mentioned above. In addition, we believe our results to be of experimental value, since they take the form of phase diagrams, which is also an uncommon feature in the available theoretical models of doped lamellar phases.

7.1 General Considerations

The phase diagrams presented in this chapter have been obtained from the prescription described in Section 6.4. Section A.6 describes in detail how the phase diagrams were generated from our numerical results and how the uncertainties in the position of coexisting phase points were determined.

7.1.1 Approximations

Since they are obtained from the Realistic Model of Chapter 5, the following results are subject to the same approximations (see Section 5.1). Furthermore, in Chapter 6 we assumed the bilayers to be flat (rigid) and composed of insoluble surfactants. In addition to the above approximations, since our model does not account for other known forces between bilayers (Van der Waals, hydration etc.), we will claim validity for our results only where these interactions are negligible compared to electrostatic and polymeric effects. The relevance of our prediction
7.1. GENERAL CONSIDERATIONS

to experimental situations in light of our assumptions will be discussed in 7.5 and Chapter 8.

7.1.2 The Salt Reservoir

As mentioned in Chapter 6.1, we shall consider a doped lamellar phase is in contact with a salt reservoir through a membrane permeable only to salt, as the phase behaviour is more easily calculated in this case.

7.1.3 Parameters Used

Table 7.1 displays the "baseline parameters" used in the calculation of the phase diagrams to follow, which, with the exception of the parameter whose variation is under investigation, were held fixed at the values shown. The values are loosely based on the experimental systems of Chapter 3: typical charged bilayers (e.g. CPC1 or SDS+alcohol) in an aqueous salt solution doped with water-soluble polymers (PVP or PEG) at room temperature [75, 83, 84, 85, 102].

The first five parameters of Table 7.1 are identical to those discussed in Sections 4.5.2 and 5.5.3 and don’t need to be commented on further. The polymer properties were also considered in Section 5.5.3. The value of $0.1 \text{ e nm}^{-2}$ ($1000 \text{ Å}^2 \text{ e}^{-1}$) used for the surface charge density $\sigma$ is slightly on the low side when compared to that used in lamellar experiments (the area per charged group $\Sigma$ is usually closer to $\approx 50 - 100 \text{ Å}^2 \text{ e}^{-1}$ [103, 83]). It is nevertheless not an unreasonable value, since the surface charge density can be diluted at will using systems with mixed charged and nonionic surfactants [84]. When studying the effect of $\sigma$, its values where chosen in the range $\sigma = 0.05 - 0.2 \text{ e nm}^{-2}$ ($\Sigma = 500 - 1000 \text{ Å}^2 \text{ e}^{-1}$), some of which overlaps with that experimentally investigated by Ligoure et al. [84] ($\Sigma = 160 - 600 \text{ Å}^2 \text{ e}^{-1}$).

The reservoir concentration of salt $c^s_r$ is also not unreasonable when compared to experiments using a dialysis membrane (Dubois et al. used reservoir concen-
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<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elementary charge</td>
<td>(e)</td>
<td>(1.6 \times 10^{-19} \text{ C})</td>
</tr>
<tr>
<td>Permittivity of vacuum</td>
<td>(\varepsilon_0)</td>
<td>(8.85 \times 10^{-12} \text{ F m}^{-1})</td>
</tr>
<tr>
<td>Boltzmann's constant</td>
<td>(k_b)</td>
<td>(1.38 \times 10^{-23} \text{ J K}^{-1})</td>
</tr>
<tr>
<td>Temperature</td>
<td>(T)</td>
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</tr>
<tr>
<td>Permittivity of ionic solution</td>
<td>(\varepsilon_1)</td>
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</tr>
<tr>
<td>Permittivity of polymer</td>
<td>(\varepsilon_2)</td>
<td>2</td>
</tr>
<tr>
<td>Dielectric factor</td>
<td>(f)</td>
<td>1.5</td>
</tr>
<tr>
<td>Polymer lattice length</td>
<td>(a)</td>
<td>10 Å</td>
</tr>
<tr>
<td>Flory Parameter</td>
<td>(\chi)</td>
<td>0.495</td>
</tr>
<tr>
<td>Number of lattice units per chain</td>
<td>(N)</td>
<td>2000</td>
</tr>
<tr>
<td>Surface charge (area per surface charge)</td>
<td>(\sigma(\Sigma))</td>
<td>(0.1 \text{ e nm}^{-2} (1000 \text{ Å}^2 \text{ e}^{-1}))</td>
</tr>
<tr>
<td>Res. salt concentration (Debye length)</td>
<td>(c^*)</td>
<td>(0.02 \text{ M (21.5 Å)})</td>
</tr>
<tr>
<td>Res. monomer volume fraction</td>
<td>(\phi^r)</td>
<td>control parameter</td>
</tr>
</tbody>
</table>

Table 7.1: Parameters used to obtain the phase diagrams

From the results of Section 5.5.5 we expect our mapped model to predict phase coexistence between lamellar phases doped with increasing amounts of polymer. When studying the effect of salt, we have used \(c^*\) in the range \(0.01 - 0.05 \text{ M}\). We should remark that experiments with doped smectics do not normally use dialysis membranes, so one should remember that the above concentrations do not correspond to the actual salt content of a lamellar phase (salt will be expelled by the Donnan effect). These matters are discussed in Section 7.5.

\subsection*{7.1.4 Expectations}

From the results of Section 5.5.5 we expect our mapped model to predict phase coexistence between lamellar phases doped with increasing amounts of polymer. In Chapter 6 we saw that this coexistence can be of two types: between lamellar phases of different periods (\(L_\alpha L_\alpha\) phase separation, as in Chapter 3) and between a lamellar phase of finite period and one, coincident with the reservoir, with an
7.2 Influence of Electrostatic Parameters

Here we study the influence of surface charge and added salt when a polymer solution of fixed properties is added to a lamellar phase.

7.2.1 Effect of Bilayer Surface Charge Density

We begin our study fixing the salt concentration in the reservoir at $c_{\text{salt res}} = 0.02 \text{ M}$ and changing the surface charge density, $\sigma$. At this reservoir concentration the salt content of the bilayers is quite high and the electrostatic interaction between the bilayers significantly screened. (The screening length in the absence of polymer would be $\lambda = 21.5 \text{ Å}$).

Density-density phase diagrams, with polymer and bilayer volume fractions as composition variables, are shown in Figures 7.1, 7.2 and 7.3 for doped lamellar phases with $\sigma = 0.05, 0.1$ and $0.2$, respectively.

We can see that, irrespective of coupling being accounted for by the model, an increase in $\sigma$ changes the phase diagram topology from a large area of L0L coex-
istence (Fig. 7.1), through an intermediate "pinch off" (Fig. 7.2, coupled case\textsuperscript{ii}), to two miscibility gaps, separated by a polymer–containing L\textsubscript{a} region (Fig. 7.2, uncoupled; Fig. 7.3, coupled and uncoupled). In the latter case, the miscibility gap on the "bilayer dilute" side of the diagram starts as L\textsubscript{a}L coexistence, where the system demixes into a pure polymer and pure bilayer phases, and, for higher bilayer concentrations, turns into a L\textsubscript{a}L\textsubscript{a} coexistence between polymer–loaded lamellars which is closed off by a critical point. The same shape is mirrored by the region extending to the more concentrated side of the diagram: the demixing begins at a critical point opening a region of L\textsubscript{a}L\textsubscript{a} coexistence between polymer–loaded lamellars. The more concentrated coexisting lamellar phase eventually becomes unable to accommodate any polymer and the L\textsubscript{a}L\textsubscript{a} coexistence is between a loaded lamellar phase and pure lamellar one.

\textsuperscript{ii}The pinch–off is not shown for the uncoupled case, but, as evidenced by the study of other parameters, it is an inevitable topological feature of the phase succession.

\textsuperscript{1}In the colour version red denotes coupling has been accounted for and blue that it hasn't. This applies to all the phase diagrams in this chapter.
7.2. *INFLUENCE OF ELECTROSTATIC PARAMETERS*

Figure 7.2: Effect of surface charge density on phase behaviour: $\sigma = 0.1 \text{enm}^{-2}$. Coupled (●) and uncoupled (○) coexisting phase points have been connected by tielines (full and broken respectively).

Figure 7.3: Effect of surface charge density on phase behaviour: $\sigma = 0.2 \text{enm}^{-2}$. Coupled (●) and uncoupled (○) coexisting phase points have been connected by tielines (full and broken respectively).
CHAPTER 7. PHASE BEHAVIOUR OF POLYMER DOPED SMECTICS

We finally notice that accounting for electrostatic coupling, as could be expected, makes no difference at very low $\sigma$, but at higher surface charge densities affects the details of the particular topology predicted. Fig. 7.2 for the case $\sigma = 0.1$ shows a striking consequence of coupling: the phase diagram displays a characteristic pinch-off in the phase diagram joining the “about to be separate” regions, absent from the uncoupled prediction. This is a clear statement: for similar parameters the predicted phase behaviour is qualitatively different for coupled and uncoupled approaches. The latter predicts two separate regions of immiscibility mentioned above, the former predicts the same regions joined by an immiscibility “bottleneck”. In the case of $\sigma = 0.2$ the same qualitative features are predicted for both approaches; however, the phase boundaries and critical points are visibly affected: in the coupled case the tips of the regions of $\text{L}_0\text{L}_0$ separation are closer together.

What’s happening: uncoupled version

As evidenced in Section 5.5.5, changing $\sigma$ changes the overall strength of the electrostatic repulsion between parallel surfaces (bilayers).

To explain the observed phase behaviour, it is useful to picture an experimental scenario: imagine preparing a mixture described by the same parameters of Table 7.1 and of a certain composition corresponding to a point in the phase diagrams shown. For example, if a mixture is prepared in the $\text{L}_0\text{L}$ region of Fig. 7.1 around $(\phi_b = 0.18; \phi_p = 0.1)$ our phase diagram predicts the system will demix into a polymer free lamellar phase with $\phi_b \simeq 3.1$ and a bilayer free polymer solution with $\phi_p = 0.2$. The demixing occurs to lower the free energy of the prepared mixture, which comprises, in the uncoupled case, separate polymer and electrostatic contributions. At the composition of the example (and anywhere the same conditions apply), the electrostatic repulsion is weak enough to make the system energetically favour a configuration where the polymer free energy is
increased through its expulsion into a more concentrated solution \[\text{iii}\] at the expense of the electrostatic repulsion which is increased as the coexisting lamellar phase is compressed to make space for the polymer (note, the whole process is constrained by the container to conserve volume).

If a mixture were prepared at higher \(\sigma\), at a point in an \(L_\alpha L_\alpha\) region of the same diagrams, the same tendencies would be at play in driving demixtion. This time, however, the repulsion is strong enough not to allow the compression of a lamellar phase to expel all the polymer and form a polymer solution. Instead, one phase is compressed as much as repulsion allows (for the total volume given) and the expelled polymer is accommodated in the coexisting phase.

**What's happening: coupled version**

There are two effects of the coupling physics which modify the phase–determining interactions: the electrostatically assisted polymer expulsion and the polymer-induced reduced electrostatic repulsion.

Such changes will only have noticeable effects for high enough field strengths \((\sim \sigma)\). Thus in Fig. 7.1 accounting for coupling makes no difference, at least for the equilibrium phase behaviour as shown. At higher \(\sigma\) the observed differences depend on the position in the phase diagram, since the difference between the coupled and uncoupled contributions depends in a nontrivial way on both on the spacing between bilayers \((\sim \phi_b)\) and the amount of polymer between them. When a mixed state is prepared as above, the demixing will have to juggle the additional coupling effects. For example, in the pinch–off region around \((\phi_b = 0.2; \phi_p = 0.02)\), in addition to the entropy diminishing confinement, the polymer free energy will pay the price of keeping a dielectric in a nonuniform field. While the confinement alone would not suffice to make phase separation favourable for the given repulsion, the dielectric contribution provides the proverbial straw

\[\text{iii}\]Since the \(\chi\) parameter is close to the theta point, the osmotic cost of expulsion is handsomely compensated by the increase in entropy.
that breaks the camel's back. In addition, the reduction of the repulsion due to the polymer permittivity makes it "easier" for the phase separation to occur (the compressibility of the lamellar phase is lowered by the polymer). Similar reasoning can be used to motivate the other observed differences in the phase diagram, such as the difference in the position of the critical points etc..

Finally, it is worth remarking that coupled effects are not most dramatic for the highest $\sigma$, as one would naively expect. The antithetic nature of the coupling is at play: expulsion is enhanced and repulsion reduced with increasing $\sigma$, but this simultaneously reduces the range in which bound phase behaviour is found, and consequently, the range over which coupling effects can be observed.

### 7.2.2 Effect of Reservoir Salt Content

Next we hold the surface charge fixed at $\sigma = 0.1 \text{ e/nm}^2$, and decrease the salt concentration in the reservoir. This provides a way of probing the effect on the phase behaviour of screening of electrostatic interactions.

Figures 7.4, 7.5 and 7.6 show the density–density phase diagrams when the reservoir contains $c'_s = 0.047\text{M}, 0.02\text{M}$ and $0.01\text{M}$ of salt, respectively.

The effect of decreasing salt (increasing the screening length) on the topological succession of phases is qualitatively the same as that of increasing $\sigma$. This is no surprise, since reducing the amount of salt increases the "range" of electrostatic repulsion over the polymer induced attraction, as we saw in Section 5.5.5. We can see the same general features arising: the $L_\alpha L$ triangular region (Fig. 7.4, coupled); the pinch–off at "early" (Fig. 7.4, uncoupled) and "late" (Fig. 7.5, coupled) stages in the topological succession; and the opposing regions of immiscibility terminating in critical points (Fig. 7.5, uncoupled; Fig. 7.6, both cases).

The relative extent of the phase regions and the changes in their shape (tieline length and tilt) appears, however, affected differently as we change $c'_s$. For ex-
7.2. **INFLUENCE OF ELECTROSTATIC PARAMETERS**

Figure 7.4: Effect of reservoir salt concentration on phase behaviour: $c_R = 0.047$ M. Coupled (●) and uncoupled (○) coexisting phase points have been connected by tielines (full and broken respectively). N.B.: the vertical scale on this diagram extends further than that of the following two.

Figure 7.5: Effect of reservoir salt concentration on phase behaviour: $c_R = 0.02$ M. Coupled (●) and uncoupled (○) coexisting phase points have been connected by tielines (full and broken respectively).
ample, the "dilute miscibility gap" (in the left corner of the diagram) shrinks considerably in size as the $c^*$ is doubled from 0.02M in Fig. 7.5 to 0.01M in Fig. 7.6 with respect its concentrated counterpart.

As when $\sigma$ was changed, we notice that coupling changes the position of the succession of phases as a function of $c^*$. In Fig. 7.4 we see how $L_\alpha L$ separation between a polymer solution and a pure lamellar phase is expected in a coupled scenario, whilst, disregarding of coupling, beyond moderate bilayer concentrations, the polymer solution causes phase separation into pure and (polymer) loaded lamellar phases. More quantitatively, where the coupled prediction does not overlap the uncoupled one, a coupled approach predicts insolubility of the polymer in the lamellar phase up to high polymer concentrations ($\phi_p \approx 0.3$), whilst the coupled approach predicts solubility above $\phi_p \approx 0.15$. The latter examples represent another clear cut difference in the prediction of the two descriptions.

Fig. 7.5 is the same as before and will not be further commented on specifically (it represents a reference diagram for all the results to follow). For $c^* = 0.01$M
(Fig. 7.6) we notice how, in the concentrated immiscibility region, the differences between the two predictions are not discernible within the errors in the determination of the phase boundaries. The differences between the predictions for the dilute miscibility gap are more marked, with a slight difference in the position of the critical points and the tilt of the tielines.

What’s happening: uncoupled version

The mechanism of phase separation is the same as mentioned when we studied the effect of surface charge density variation: the free energy of the mixture is minimised by suitably arranging the polymers and the bilayers (and the ions).

As shown in Section 5.5.5, the effect of removing salt from the reservoir increases the “range” of the effective interaction between the bilayers, while the polymer contribution in obviously uninfluenced by the amount of salt. This has the same effect as increasing $\sigma$: the repulsive contribution increases. The phase behaviour will have the same broad features as we decrease in $c_s^r$.

There will be differences in the details of the succession, however, which reflect the difference associated with changing the range as opposed to changing the magnitude of a repulsive interaction against the same attraction. It is not a trivial task to make hand-waving arguments to explain the phase diagrams in terms of these observations.

What’s happening: coupled version

As explained in the case of $\sigma$, the differences between coupled and uncoupled approaches for each phase diagram are due to electrostatically assisted polymer expulsion and polymer–induced reduced electrostatic repulsion. For example, around $\phi_b = 0.25$, $\phi_p = 0.15$ in Fig. 7.4, $L_\alpha L$ phase separation can occur in the coupled case, because of the enhanced expulsion mentioned earlier. In the

\[IV\] The reduction of the electrostatic repulsion is not a dominant effect for such high salt concentrations.
uncoupled case, polymer cannot be so easily expelled, so it is forced to stay in one of the phases and the favoured phase separation is $L_\alpha L_\alpha$, as observed.

### 7.3 Influence of Nonelectrostatic Polymer Properties

The parameter study so far has been performed with the polymer solution properties held fixed. Next we investigate the effect of a nonelectrostatic polymer property: the $\chi$ parameter of the polymer solution between bilayers. The effect of electrostatic polymer properties (determining the strength of the electrostatic coupling) are left to Section 7.4. (Time does not allow to study the effect of changing the lattice length $a$, the type of lattice, or the number of lattice monomers $N$).

#### 7.3.1 Variation of the $\chi$ Parameter

With all other parameters held fixed as before, we consider three different polymers for which water is, respectively: a poor solvent with $\chi = 0.515$ (Fig. 7.7); a near theta solvent with $\chi = 0.495$ (Fig. 7.8, the "reference" system); and a good solvent with $\chi = 0.3$ (Fig. 7.9).

Decreasing $\chi$ in the range shown has broadly the same effect of an increase in $\sigma$ or a decrease in $c_s^*$: merged $L_\alpha L$ and $L_\alpha L_\alpha$ regions (Fig. 7.7, both cases) shrink (Fig. 7.8, coupled) and split into separate dilute and concentrated miscibility gaps (Fig. 7.8, uncoupled). Finally, the dilute miscibility gap disappears and only the concentrated gap is left (Fig. 7.9, both cases).

The phase succession, seems, however, to be captured at different stages and we expect the phase boundaries to be different since changing $\chi$ affects both the magnitude and the range of the polymer contribution to the interactions. Notice,
in addition, that the boundary of the concentrated miscibility gap is vertical, appearing to denote a saturation in the bilayer volume fraction of the polymer loaded phase.

![Diagram showing coupled and uncoupled phase points](image)

**Figure 7.7**: Effect of polymer solution $\chi$ parameter; $\chi = 0.515$. Coupled (•) and uncoupled (○) coexisting phase points have been connected by tielines (full and broken respectively).

The differences between coupled and uncoupled approaches are greater for the higher values of $\chi = 0.515, 0.495$. Figures 7.7 and 7.8 show how the differences are more pronounced on the bilayer–dilute side of the phase diagram. Once again the coupling increases the extent of the L$_\alpha$L region with respect to the uncoupled case. Where L$_\alpha$L$_\alpha$ coexistence kicks in, the polymer–loaded phase can accommodate more polymer in the coupled case, though this difference gets dwarfed for more concentrated lamellar phases. No major differences in the phase behaviour are detectable for $\chi = 0.3$ (Fig. 7.9).

**What's happening: uncoupled version**

It was discussed in Section 5.5.5 how, in an uncoupled scenario, changing the $\chi$ parameter will affect the strength and range of the polymer (which also depend
Figure 7.8: Effect of reservoir salt concentration on phase behaviour: $\chi = 0.495$. Coupled (●) and uncoupled (○) coexisting phase points have been connected by tielines (full and broken respectively).

Figure 7.9: Effect of reservoir salt concentration on phase behaviour: $\chi = 0.3$. Coupled (●) and uncoupled (○) coexisting phase points have been connected by tielines (full and broken respectively).
7.3. **INFLUENCE OF NONELECTROSTATIC POLYMER PROPERTIES**

on the concentration of the polymer solution, but clearly not the electrostatics).

At the same polymer concentration, the polymer osmotic pressure is biggest for good solvents ($\chi = 0.3$), since monomers interact more strongly. For the same reasons, however, a good solvent efficiently screens any entropy-reducing perturbations, so that the expulsion necessary for this increased pressure to win over the electrostatic repulsion will only happen at small lamellar separations (high $\phi_b$), when the polymer can "sense" its confinement. For *theta* solvents the screening is such that correlations extend over larger distances. Polymer can be expelled at large lamellar separations. The situation is similar for poor solvents, though these exert slightly less pressure and the correlations are ever so slightly increased by the mutual attraction between the chains.

With these considerations in mind we see that the $L_\alpha L$ phase separation in the dilute region for poor or *theta* solvent cases occurs because the polymer correlations extend to large distances, causing an attraction sufficient to overcome the weak electrostatic repulsion (reduced at large distances for the reasonably short screening length considered).

As the bilayers are made more concentrated the electrostatics is stronger so that the same amount of polymer (with the same range and strength) is unable to balance the electrostatics. $L_\alpha L_\alpha$ separation will be observed with polymer entering the lamellar phase of larger smectic period.

For a good solvent the range of the polymer-induced attraction is too short to phase separate dilute samples and only the concentrated miscibility gap is observed. The vertical binodal\(^v\) indicates that the polymer loaded phase can be compressed no further regardless of its polymer content. This is because of the high osmotic pressure associated with a confined polymer solution in a good solvent, even at low polymer concentrations. A similar saturation is expected in the other phase diagrams presented in this chapter, but, since large values of $\chi$ were used in these cases, the saturation should occur at high polymer concentrations.

\(^v\)Binodal is synonymous to phase boundary.
What's happening: coupled version

Since high values of $\chi$ imply smaller screening of any disturbance to the polymer concentration profile, coupling effects will be greater for $\theta$ or poor solvents than for good solvents. Screening, however, also depends on the polymer concentration, so that differences in the phase behaviour predicted by the coupled approach depend on the location on the phase diagram.

As for the previous parameters, coupling generally extends the size of the demixing regions. For poor or near-$\theta$ solvents electrostatically assisted expulsion and repulsion reduction will make phase separation favourable over a wider area in the bilayer-dilute part of the phase diagram. The differences disappear in the bilayer-concentrated part because the influence of electrostatics on the polymer has a shorter "range" given the larger polymer concentrations required to balance the increased electrostatic repulsion.

Similarly to the uncoupled scenario, no amount of polymer is sufficient to cause phase separation in the case of good solvents, since the range of the attraction is too short.

### 7.4 Effect of Coupling Strength

To conclude our parameter study we shall consider the dependence of the phase behaviour on the "coupling strength", i.e. the extent by which electrical polarisation causes the polymer physics and the electrostatics to be interdependent. Such strength is controlled by the dielectric contrast and the polarisable volume, as we saw in Section 5.4.2. The expectation is that as the coupling is made small, by either decreasing the dielectric volume or the dielectric contrast, the phases predicted in the uncoupled limit will be recovered.
7.4. EFFECT OF COUPLING STRENGTH

The influence on the phase behaviour of $f$, the factor which governs the amount of polarisable material associated with a lattice monomer, is shown next. Unfortunately time did not allow investigation of the effect dielectric contrast, but in light of the results of Section 5.5.5 we expect the same qualitative features for the effect of $f$.

7.4.1 Effect of dielectric monomer size

Shown in Figures 7.10, 7.11 and 7.12 are the phase diagrams calculated when $f = 1.1$, $f = 1.5$ and $f = 2$ respectively. As expected, an increase in $f$ gradually reduces the differences between coupled and uncoupled approaches, the differences being more pronounced in the bilayer dilute regions, except for $f = 1.1$ (Fig. 7.10). In the latter case, the contrast between the two descriptions is stark. In the dilute region the $L_aL_a$ coexistence predicted by the uncoupled model is replaced by a significantly larger area of $L_aL$ in the coupled case. Particularly noteworthy is that for this value of $f$ (strong coupling), the coupled prediction for the bilayer concentrated branch of the upper binodal does not “diverge” like the uncoupled one. This, as also indicated by the visibly different tilt of the tielines, indicates a major effect of the coupling on the polymer content of concentrated phases which we shall soon discuss.

Increasing $f$ to 1.5 and 2 progressively irons out the differences between the coupled and uncoupled predictions. It is worthy of note that, even for the reasonable\textsuperscript{vi} value of $f = 2$ (the dielectric sphere diameter is equal to the lattice length), the “critical pinch–off” is preserved.

*What’s happening*

The differences between coupled and uncoupled predictions can be explained as has been done for the previous parameters studied.

\textsuperscript{vi}Reasonable in the sense explained in Section 5.5.3.
Figure 7.10: Effect of the dielectric size factor $f$: the case $f = 1.1$ discussed in the text. Coupled (•) and uncoupled (○) coexisting phase points have been connected by tielines (full and broken respectively).

Figure 7.11: Effect of reservoir salt concentration on phase behaviour: $f = 1.5$. Coupled (•) and uncoupled (○) coexisting phase points have been connected by tielines (full and broken respectively).
It is interesting to discuss the bilayer concentrated behaviour for $f = 1.1$. It was noticed from the pressure profiles of Section 5.5.5 that both expulsion and dielectric reduction of the electrostatic repulsion are extremely pronounced for this parameter. The reduction of the electrostatic repulsion implies that for strong confinement (large bilayer volume fractions) the phase separation will be between phases with a larger difference in spacing than in the uncoupled case. This is because, for strong coupling, the dielectric screening of the polymer contributes significantly to reducing the electrostatic repulsion between bilayers, so that the pressure of the polymer-loaded phase needs to be balanced by a greater electrostatic repulsion.

Finally the fact that for $f = 2$ the pinch–off is still present for the coupled case is because the pinch–off is a merger of two "dilute" critical points, where we have seen the difference between approaches is most evident.
7.5 Relevance to Real Systems

At this point we need to ask ourselves what relevance the phase diagrams of this chapter have to those obtained experimentally, e.g. the doped smectics of Chapter 3 (in particular the investigations of the Bordeaux [85] and Montpellier [75, 83, 84] groups). Before doing this, however, mention must be made of how the use of a salt reservoir affects the results, so that a comparison with the most common experiments can be made.

Differences Due to the Salt Reservoir

The lamellar phases in the experiments of Chapter 3 do not contact a salt reservoir. A certain amount of salt is added to a sample and, if phase separation occurs, such salt is expected to partition between phases just like the polymer.

When comparing experimental results to those calculated assuming a salt reservoir one has to correct for the fact that the salt content of a phase, fixed in experiments, is unconstrained in the calculation. With a membrane and reservoir in place lamellar phases can expel salt into the reservoir in a proportion which depends on the separation between bilayers (the Donnan effect of Section 2.2.3) reducing the repulsion between them. For a system of fixed salt content this expulsion is not possible\(^{\text{vii}}\) and we expect a greater repulsion between bilayers. We can consequently deduce that more polymer will be required to cause phase separation in a fixed salt system. From this, it is clear that the coexisting phases will in general be differently positioned to those predicted with a reservoir in place. The phase diagrams at fixed salt can be imagined as obtainable from the reservoir results via a stretching of the polymer axis \((\phi_p)\) and a similar deformation of the bilayer axis \((\phi_b)\) (whose details are hard for us to predict from simple considerations).

\(^{\text{vii}}\)The system is its own reservoir: the expulsion amounts to a partitioning of the salt between coexisting phases.
7.5. RELEVANCE TO REAL SYSTEMS

Ligoure’s group [75] numerically evaluate the salt content of a lamellar phase of fixed polymer content. Our model allows similar evaluations to be performed\textsuperscript{viii}; however, the problem of the calculation of phase diagrams for fixed salt content, though conceptually simple, appears cumbersome to implement considering how our model has been set up.

Unfortunately, the experiments reported by the group at Bordeaux (Section 3.1.2) do not mention salt at all; we shall assume below they have been treating a “saltless” solution (though even in the cleanest experiment, a solution is never truly saltless, and will contain, at the very least an amount of be decomposed water molecules, depending on the solution’s pH).

Comparison with Experimental Results

Irrespective of an account for dielectric coupling, our results appear to reproduce several of the main qualitative features observed in experiment.

The phase coexistences we predict are those observed in experiments: lamellar–lamellar and lamellar–isotropic. However, since we do not expect our model to be accurate where the physics of surfactant self-assembly needs to be considered, we assume that our results are inapplicable to the features of very dilute and very concentrated lamellar phases, e.g. the isotropic lamellar coexistence at high $\phi_b$ of Fig. 3.1. Such features are indeed not predicted in the results of this chapter. Another feature which does not appear in our results is the “closed–loop” observed by the Bordeaux group Section 3.1.2. Sear has theoretically calculated a phase diagram with a closed–loop for doped smectics, plausibly attributing its occurrence to the existence of two repulsions of different ranges, the electrostatic and the hydration interactions between bilayers, competing with the polymer induced attraction [76]. For short distances between bilayers (large bilayer volume

\textsuperscript{viii}In fact, together with the data used to construct the diagrams of this chapter, we have also gathered values of the salt content of coexisting phases. These are not presented because of time and length constraints.
fraction) hydration is thus responsible for “closing the loop”, as it limits the polymer induced attraction between bilayers. In this picture, a model with no short ranged repulsion such as ours cannot predict closed loops, but only “divergent” binodals.

The experimental trends discussed in Section 3.1.1 also seem to follow from our model. For example, as observed by Ligoure et al. (see Section 3.1.1), for a fixed polymer and bilayer volume fraction, progressive addition of salt or reduction of charge cause a transition from a monophasic lamellar sample to a coexistence between lamellar phases of different periods (bilayer concentration). As an example of the latter case (valid for both coupled and uncoupled scenarios), consider our prediction for the phase behaviour of a system with $\phi_b = 0.25, \phi_p = 0.02$ as $\sigma$ is decreased from 0.2 (Fig. 7.3) to 0.1 enm$^{-2}$ (Fig. 7.2).

Considering that the parameters used to calculate our phase diagrams are not too dissimilar from those used in experiments, the values defining the phase boundaries appear to be of the right order of magnitude. In view of the earlier considerations on the effect of the reservoir, and accounting for the fact that we have been using small surface charge densities and large salt concentrations (with respect to “salt–less” systems), we might expect the characteristic phase features to occur at smaller polymer concentrations with respect to experiments.

Finally, with regards to the effect of coupling, it is hard to contrast our predictions with any existing experiments, we leave a discussion of suggestions for future experiments designed at investigating the effect of coupling to Chapter 8.

### 7.6 Concluding Comments

We hope to have convinced the reader of the value of the framework developed in earlier chapters as an instrument to study the qualitative features of the phase beh

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(ix) For the reasons given in Chapter 8 we do not in general expect quantitative accuracy from our model.
7.6. CONCLUDING COMMENTS

Behaviour of polymer-doped smectics and the effects of parameter variation. When coupled and uncoupled predictions are contrasted, our results indicate, if our approximations are sufficient to allow a realistic description in the admittedly limited parameter space explored, that an account of electrostatic coupling is necessary to correctly describe the behaviour of polymer doped smectics, except, perhaps, in the case of good solvents. We should also add that, although our results indicate it is important to include coupling to accurately describe the phase behaviour, this inclusion does not qualitatively modify the "trends" in the topological succession of phase diagrams in response to parameter changes. Despite this, there are some parameters for which coupled and uncoupled predictions are found to be qualitatively different, such as Fig. 7.2. Further, beneath the similarity between phase diagrams, other features are modified by the coupling, such as the monomer concentration profiles, with a pile up of polymer near the midplane (Fig. 5.4c). Such features might be experimentally detectable.

The above considerations will be further elaborated upon in the chapter concluding this thesis (Chapter 8), together with suggestions for future experiments attempting to isolate "dielectric effects" and speculation on some interesting topics which we have not had time to investigate.
Chapter 8

Conclusions and Outlook

This thesis has argued that the electrically active nature of "fatty" solutes should affect their distribution about charged surfaces, and so modify the force between them. Such a point of view is not widely held by the soft matter community (which has, however, recently started to become aware of closely related effects, as we saw in Section 2.6.3). On one hand this is likely to be a result of the incorrect assumption that neutral solutes of "sub-colloidal" (but supramolecular) dimensions are not affected by electrostatics because they don't carry any charge. On the other, it is perhaps a consequence of the fact that such effects are often only subtly manifest in the relevant experiments which have been carried out so far (with the possible exception of L. Galloway's experiments, as we shall soon discuss).

In the theoretical analysis of the preceding chapters, we have shown, for a range of realistic conditions, that the dielectric proprieties of uncharged solutes significantly influence the force between charged surfaces and, of consequence, the phase behaviour of charged macroions, such as smectics. Such an analysis has not been previously carried out, to the best of our knowledge.

Below, we present several suggestions for the experimental assessment of the non-additivity of electrostatic and polymeric interactions in determining the phase
behaviour of doped lamellar phases. To conclude, a few thoughts on some other interesting questions raised by our work, which time restraints have not allowed us to pursue, but might interestingly be followed up by future investigators.

**Suggestions for Future Experiments**

The basic notion that neutral solutes respond to electric fields appears very reasonable. The phase diagrams presented in Chapter 7 also appear to produce sensible results (subject to the limitations mentioned in Section 7.5). Considering the approximations made to construct our model, however, we could not blame the reader for being skeptical about our results on the importance of coupling. As always, theoretical conjectures need to be experimentally assessed.

In Section 7.5 we hinted at the difficulties inherent in detecting dielectric coupling effects by performing experiments with doped lamellar phases as they have been carried out so far. It could, nevertheless, be possible to devise future experiments attempting to isolate any “dielectric effects”, with the guidance of our model or a slightly more sophisticated version of it.

As it stands, we expect our model to be most accurate when used to predict of the phase behaviour of rigid bilayers mixed with a polymer solution at, or near, the *theta* point, and small concentrations of monovalent electrolyte provided from a salt reservoir which contacts the system through a dialysis membrane\(^1\) Thus, If experiments were possible for these conditions, then the predictions of our model could be checked for agreement with the observed phase behaviour in response to parameter variation.

We believe, however, that the most likely value of our work, for anyone wishing to investigate the effects of dielectric coupling experimentally, is that of a “qualita-

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\(^1\)This is because our phase diagrams have been obtained in a framework adopting the Poisson–Boltzmann and Flory–Huggins + square gradient mean field descriptions, with the additional smoothing approximation for the description of dielectrics, the assumption of approximately rigid bilayers (to avoid any effects of bilayer fluctuations) and the requirement of a salt reservoir in contact with the smectics.
tive guide" to the consequences of such effects on phase behaviour. For example, our predictions show that the effects of coupling are most manifest around the critical points of the concentrated miscibility gap in the phase diagrams; an experiment could then be devised which used polymers with differing amounts of polarisable groups or permittivity to check for any sensitivity on the location of the critical point on these parameters. On a related note, since the presence of the dielectric changes the shape of the force between surfaces, experiments could also be devised to measure the compressibility of a lamellar phase (as in [87]).

Suggested Improvements

Model II is realistic, but could benefit from some improvements. The Flory–Huggins mean field description of the polymers, for example, could be replaced by a more accurate scaling description [74]. In addition (or alternatively), the polymer could be made adsorbing or charged. The latter cases are of particular interest. An adsorbing polymer may, in fact, because of "electrostatic depletion" behave like a nonadsorbing one, provided the energy of adsorption is always lower than the electrostatic cost of keeping the polymer at the charged surface. Similarly, a polymer carrying small amounts of charge of opposite sign to the surface will want to adsorb, but the adsorption might be reduced or countered by dielectric depletion.

When applied to doped smectics, other interactions, such as hydration forces could also be included in the model. Before complicating matters by introducing new physics, however, some insight might be also gained in trying to make some of the handwaving considerations of Chapter 5 more quantitative, through simple "order of magnitude" considerations applicable to appropriate limiting solutions of the equations of Model II.
Loose Ends

Several other questions relating to the consequences of dielectric coupling have been raised, more or less explicitly during this thesis.

The effect of the curvature of a charged surface is also of particular interest. The so-called Derjaguin approximation [104], often used to treat colloidal interactions, allows to map the interaction between flat surfaces to that between charged spheres, provided the range of the interaction is much smaller than the radius of the spheres. Since the largest interaction lengthscale of the flat plates of Model II is \( \sim \) nm (as determined by the electrostatics, whose “range” is not drastically modified by the coupling), it would be interesting to use the Derjaguin approximation to evaluate the force between charged colloids or between the surfaces of a surface force apparatus, immersed in a concentrated polymer solution\(^\text{11}\). Such an application would be interesting, since the Derjaguin approximation states that the force between curved surfaces goes like the free energy of the parallel plate system, not like its osmotic pressure; this will have implications for the phase behaviour of charged colloidal suspensions.

Another interesting effect of curvature may arise precisely under the conditions where the Derjaguin approximation is not valid: when the range of the interaction between curved surfaces is comparable with the relevant radii of curvature. In this case, the long range of the interaction requires the full three dimensional (vector) nature of the electric field needs to be considered. For the specific case of colloids approaching each other, for example, curvature should cause the electric field at the symmetry plane between the colloids to have a nonzero tangential component. The field is thus nonuniform in more than one direction, which could enhance the electrostatic depletion of dielectrics. A careful development of such arguments could be used to try and explain the strange phase behaviour observed by L. Galloway (see Section 3.2.1): in this picture, it is because of electrostatically assisted

\(^{11}\text{As has been done by Borukhov et al. [105] for the case of polyelectrolytes between charged surfaces.}\)
depletion (and the intrinsically connected dielectric reduction of repulsion) that aggregates form at smaller surfactant concentrations than expected.

In general, the use of micelles, as polymers or otherwise, should definitely be relevant to experiments wanting to probe the dielectric effect, since micelles are naturally water soluble, but contain a lot more “oily” (low permittivity) material than normal water soluble polymers.

Final Words

We hope our work will stimulate further investigations (especially experiments!) on the non-additivity of electrostatic and depletion interaction in the presence of dielectric contrast. More generally, we hope to have convinced the reader that electrostatics plays an important role in the physics of soft matter, whether its constituents are charged or not.
Appendix A

Numerics and Phase Diagram Construction

In this Appendix we describe the numerical algorithms by which we solved the differential equations of Chapter 4 and Chapter 5, and how other relevant quantities were obtained from their solutions. The associated uncertainties are evaluated for each of these quantities. We also report some of the checks of the solutions which have been performed by solving appropriate limiting cases analytically or using MAPLE.

Finally we explain how the phase diagrams of Chapter 7 were produced, and what uncertainties were introduced in this process.

A.1 General Considerations

A.1.1 Boundary Value to Initial Value Problem for Our Case

In both Chapters 4 and 5, we are faced with a boundary value problem (BVP): we want to solve a differential equation (DE), or a system of these, knowing values
of the function to find or of its derivative, but not at the same point in space\(^1\). The standard methods to solve the BVPs usually involve shooting or relaxation methods [92].

Here, however, since we are not interested in a solution for a particular value of interplate \(H\), but in obtaining solutions for a range of \(H\)s, we have implemented our own method of solution (a kind of unconstrained shooting method).

In a nutshell, our method involves solving an initial value problem at the same point in space (the plate surface) by guessing the unknown value/-s of the initial conditions and sweeping them over a range of guesses. To each of these guesses corresponds a particular \(H\), as will be made clearer below. The initial value solution of the differential equations was found using the standard Runge–Kutta fourth order method [92], which has a local truncation error for the solutions of \(O(l^5)\), where \(l\) is the integration step which advances the DE solutions.

### A.2 Simple Model Numerics

The DE to be solved in the simple model of Chapter 4 is Equation (4.27):

\[
\frac{d}{dX} \left( (1 - A e^{-B W^2}) \frac{dW}{dX} \right) = W
\]

subject to the boundary conditions:

\[
W|_{X=0} = W_{s1} \quad \text{(unequal potentials)}
\]

\[
W|_{X=H} = W_{s2}
\]

\[
W|_{X=0} = W_s = W|_{X=H} \quad \text{(equal potentials)}
\]

\(^1\)contrast this to initial value problems (IVP) where the DE propagates the solution forward from initial conditions specified at a the same point.
we can turn this into an initial value problem by rewriting the boundary conditions as follows:

\[
\begin{align*}
W|_{x=0} &= W_s \quad \text{(A.1)} \\
\frac{dW}{dX}|_{x=0} &= -G \quad \text{(A.2)}
\end{align*}
\]

where \( G \) is the unknown value of the surface field. The boundary conditions (A.2) and (A.2) apply to both the equal and unequal surface potential cases, since changing the value of \( G \) we can sweep all solutions smoothly from one case to the other.

### A.2.1 Solutions, Interplate Spacing and Osmotic Pressure

We then solve Equation (4.27) for a range of values of \( G \) for a given set of parameters of the model. This range covers both equal and unequal potential solutions. According to the case of interest the solutions are then searched for the separation between the plates: we look for the value of \( X \) at which each potential reaches a preset value (within a certain tolerance). The preset potential value is the initial surface potential in the case of equal potentials, or a fraction of it in the case of unequal potentials. The value of \( X \) at which these values are reached is separation \( H \) between the plates. The tolerance is a small number so the error in the separation estimate can be roughly estimated to be \( \sim l \), the integration stepsize.

By looking for the values of the potential and the field where the number of steps is half of the value at which \( H \) is found, their values were also found at the midplane at \( H/2 \). From these the osmotic pressure is found using Equations (4.35) and (4.36).
A.2.2 Uncertainties in Separation and Osmotic Pressure

We saw how the uncertainty $\Delta H$ in the interplate separation is given by the integration stepsize: $\Delta H \sim l$. The uncertainty in the osmotic pressure can be worked out from this considering the pressure is a function of $H$, as we will show in the case of Model II (Section A.4.2). We should note here that the method introduced here of evaluating the midplane quantities explained just above causes the uncertainty of the midplane quantities (and consequently on the pressure which is derived from them) to depend on the separation for small separations. This is a small effect compared to the uncertainty in pressure deriving from $\Delta H \sim l$.

A.3 Checks on Model I Numerics

Comparison with Analytic Limits

An easy check on the numerics can be performed by comparing the numerical solutions obtained from our algorithm with the analytic limit solutions when the constants $A$ or $B$ (defined in Chapter 4) are zero. Such a comparison is shown in Fig. A.1 for the case of the osmotic pressure.

![Figure A.1: Here we compare the limits $A = 0$ and $B = 0$ of the numerical solution with the analytical solutions available.](image)
A.4. **MODEL II NUMERICS**

We see that in these limiting cases the osmotic pressure curves agree well within the experimental error (of the order of the size of a point).

**Comparison with Numerical Solution by Maple**

Another straightforward check of the results is to solve the same differential equation using an alternative numerical method. Mathematical software such as Maple or Mathematica can numerically solve nonlinear ODEs using built in algorithms which are the same as what we used. Maple solutions have been checked against our numerics and agreement has been found, as expected (we do not show this here, but the results are analogous to those shown in Section A.5.1 for the solutions of Model II).

**A.4 Model II Numerics**

Model II of Chapter 5 is more complicated to implement. Recall the equations we need to solve are the following:

\[
\frac{d}{dX} \left( \varepsilon_e(\Psi) \frac{dW}{dX} \right) = \sinh W \quad \text{(A.3)}
\]

\[
\mathcal{C} \frac{d^2 \Psi}{dX^2} = \mathcal{B} \left( \frac{dW}{dX} \right)^2 \frac{\Psi}{(1 + A\Psi^2)^2} + \Psi \ln(\Psi^2) - \Psi \ln \left( \frac{1 - \phi^r \Psi^2}{1 - \phi^r} \right) - \mathcal{D}(\Psi^3 - \Psi) \quad \text{(A.4)}
\]

subject to the boundary conditions:
\[ \frac{dW}{dX}_{X=0} = -F_0 \]  
\[ \frac{dW}{dX}_{X=H/2} = 0 \]  
\[ \Psi_{X=0} = 0 \]  
\[ \frac{d\Psi}{dX}_{X=H/2} = 0 \]

where all the symbols have been defined in Chapter 5. Making (A.5)–(A.8) into an initial value problem (where the value of all unknown function is known at \( X = 0 \)) we write:

\[ W_{X=0} = G_1 \]  
\[ \frac{dW}{dX}_{X=0} = -F_0 \]  
\[ \Psi_{X=0} = 0 \]  
\[ \frac{d\Psi}{dX}_{X=0} = G_2 \]

Where \( G_1 \) and \( G_2 \) are unknown values which we guess.

Previously it was sufficient to sweep \( G_1 \) over a range of values, since this would univocally identify a separation \( H \). Now, however, once we have chosen \( G_1 \), we need to find the value \( G_2 \) which yields solutions with the same \( H \). The DE solving code was suitably modified to perform this task, and is described in the next subsection.

Once the equations are solved, there are derived quantities that we are interested in evaluating from their solutions (with the construction of phase diagrams in mind). The calculation of these quantities involves numerical integrations, which we have implemented using the trapezoidal approximation.
A.4. MODEL II NUMERICS

A.4.1 Matching Algorithm

To find the value $G_2$ giving solutions corresponding to the same $H$, it was required that for a given surface potential, $G_1$, and polymer square-root concentration derivative, $G_2$, the solutions have coinciding extrema for the same distance $X$ from the surface (the midplane $X = H/2$).

The search was implemented by adding a feedback to the DE solver to flag current and past information about the solutions when salient features are found (by salient feature we mean extrema, inflections or divergent behaviour). Such flags are output to the main code where corrective actions can be taken to make $G_2$ converge towards the successful value (the one giving coincident extrema at the midplane). To find coincident extrema, the code looks for the value $X$ at which both derivatives $W'(X)$ and $\Psi'(X)$ change sign. Fig. A.2 schematically illustrates the matching scenario for two different values of the integration step $h$:

![Diagram illustrating matching scenario](image)

Figure A.2: A match is found: $V(x)$ and $\psi(x)$ have extrema at the same value $x_i = H/2$ (to within an integration step $h$)

Note that, when plotted or integrated, all functions were evaluated up to the midplane value only (the rest of the function is easily determined since it has to
obey the symmetry of the problem). The reason for this is that the problem has been formulated with a constraint at the midplane. Solutions evaluated beyond the midplane would be inaccurate due to the nonlinearity of the equations: for example, there is no numerical constraint to force the polymer concentration to vanish at the far surface.

**Solutions, Spacing and Osmotic Pressure from a Successful Match**

When a successful match is found the current value of the mplane separation $H/2$ is evaluated as $H/2 = X_i - l/2$ where $X_i$ is the current value of the $X$ at step $i$ and $l$ is the size of the integration step. Similarly the midplane potential $V(H/2)$ is assigned to the current value of $V$ and the same is done for the midplane polymer concentration $\Phi(H/2) = \Psi^2(H/2)$ and other quantities of interest.

With the values of $V(H/2)$, $\Phi(H/2)$ for a given $H$, we can evaluate the osmotic pressure using Equation (5.44).

By stepping $G1$ over a range of values we can obtain solutions for different separations (we don’t know the relation between $H$ and $G1$, but we know that the lower $G1$ the larger $H$). For each parameter set, thus, a range of surface potential values was defined, corresponding to a range of separations, which could then be adjusted to suitable values.

**Net Polymer and Salt Concentrations**

We saw in Chapter 6 how the net polymer and salt concentrations inside a lamellar phase at a given lamellar separation are evaluated from the following integrals:

$$
\phi_p = \frac{1}{D+\delta} \int_0^D \phi_p(x) dx
$$

$$
n_s = \frac{n_s^r}{D+\delta} \int_0^D e^{-eV(x)/T} dx
$$
The expressions were evaluated numerically using the trapezoidal rule [106]. Writing the integrals using dimensionless variables and expressing them as twice the midplane integrals (for the reasons given in Section A.4.1), we have:

\[ 2 \int_0^{H/2} F(X) dX \approx \sum_{X_i+1 < H/2} (F_{i+1} + F_i)(X_{i+1} - X_i) \]  
(A.15)

where \( F_i \) in our case is the numerical value of either \( \Phi_p(X_i) \) or \( e^{-W(X_i)} \) at position \( X_i \) as evaluated from the solution of the differential equations (A.3) and (A.4). The subscript to Equation (A.15) indicates that the sum is stopped once the midplane \( H/2 \) is reached.

A.4.2 Associated Uncertainties

We see from Fig. A.2 that the uncertainty of the match depends on the integration step: the midplane separation is thus known to within an integration step \( l \). The total separation \( H \) between the plates thus has an uncertainty \( \Delta H \sim 2l \), associated with it. This uncertainty determines the uncertainties in the midplane values of the potential \( V_{H/2} \) and polymer concentration \( \Phi_{H/2} \), as is also evident from Fig. A.2. In fact, the uncertainty of any function of \( H, F(H) \), depends on \( \Delta H \) and can be estimated as:

\[ \Delta F \sim F(H + \Delta H) - F(H) = F(H + 2l) - F(H) \]  
(A.16)

Uncertainty in the Osmotic Pressure

Knowing the uncertainty in the net osmotic pressure \( \Delta \Pi^{net} \), introduced by the matching algorithm, is of particular interest. It can be evaluated using relation (A.16). However, since our code does not allow to choose specific values of \( H \), we can alternatively estimate \( \Delta \Pi^{net} \), by plotting \( \Pi^{net} \) with horizontal errorbars
of length $\Delta H \sim 2l$, each side of a point. This displays the accuracy with which $\Pi^{\text{net}}$ is known. We can best see this by connecting the "upper" and "lower" extremities of the errorbars to define a "tube of uncertainty" around the results for $\Pi^{\text{net}}(H)$ (Fig. A.3).

We see that for $\Delta H \sim 0.006$ (corresponding to a typical integration step $l \sim 0.003$), $\Delta \Pi$ is of the order of the data point size. In Section A.6 on the phase diagram construction we shall see that the uncertainty introduced in that process is always larger than this, so we need not estimate $\Delta \Pi^{\text{net}}$ each time we plot $\Pi^{\text{net}}$.

### Uncertainties in Polymer and Salt Concentrations

We saw in Section A.4.1 how the net polymer concentration and salt concentrations are found using the trapezoidal approximation to an integral. The uncertainties in these quantities are the error associated with replacing the integral with a discrete sum of trapezoidal slabs and the error $\Delta H$ associated with the evaluation of the upper integration limit (the separation $H$). The latter is clearly the dominating contribution since it can be estimated as $f(H/2)\Delta H/2 = O(l)$ where $f(H/2)$ is the midplane value of the function being integrated. Pictorially this uncertainty is a whole slab of thickness $\Delta H/2$ and height $f(H/2)$ centered on the midplane and this is clearly bigger than the net difference in area between the function and its trapezoidal approximation. We can thus estimate the error in the polymer and salt content of a lamellar phase in the same way as we did for the osmotic pressure: we draw a tube of uncertainty around the results for $\phi_p(H)$ and $n_s(H)$ defined by horizontal error bars $\Delta H \sim 2l$ (Fig. A.4).
Figure A.3: Plots displaying the magnitude of the uncertainty in the osmotic pressure $\Pi_{\text{net}}$. The errorbar size is $\Delta H \sim 0.006$ for (A) and $\Delta H \sim 0.025$ for (B). The above curves were obtained using the parameters of Table 5.1, except for the reservoir salt concentration and $\chi$-parameter: here we used $c^* = 0.047 \text{ M}$ ($\lambda = 14 \text{ Å}$) and $\chi = 0.3$. 
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A.5 Checks on Model II Numerics

A.5.1 Comparison with Numerical Solution Using Maple

Another way to check the numerics is to compare solutions with those found using maths packages such as Maple.

Uncoupled Model Vs. Maple for a Fixed $H$

Presented in Fig. A.5 is such comparison for the model's solutions for $H = 3.88$ (for the same parameters as the previous graphs of this chapter).

![Figure A.5: Comparison between the uncoupled solutions using our numerical routine and that built in MAPLE. Left to right: electrostatic potential and polymer concentration profiles between plates. The above curves were obtained using the same parameters as in Fig. A.3.](image)

The final steps of our numerics have been omitted to reveal the agreement with the Maple solution (solid curve).

Salt and Polymer Concentration Profiles

Next a useful comparison is provided evaluating the average salt concentrations as a function of separation.
Fig. A.6 displays the salt concentration profiles as the Poisson–Boltzmann solution is approached. This limit is then compared with the profile evaluated using Maple.

A.6  Phase Diagram Construction

As explained in Chapter 6, it is possible to construct phase diagrams of polymer-doped lamellar phases from our model. Phase coexistence can be found solving the equilibrium conditions (6.18) and (6.19) numerically, or using a graphical method. Because of the ad hoc nature of our numerical algorithms we chose to construct the phase diagrams graphically, using the equal area construction as described in Section 6.4.1.

Below we indicate, in the form of a list, the practical procedure by which the phase diagrams were obtained.

A.6.1  Preliminaries and General Features of the Procedure

- The physical parameters for the phase diagram under study are set to the desired values for solution by our numerical code.

- the control parameter (reservoir polymer concentration $\phi^r$) is set to an arbitrary (reasonable) value, e.g.: $\phi^r = 0.1$.

- The range of surface potential guesses and the limits of the integration are adjusted to yield the appropriate range of lamellar surface separations where the solutions were found for the given parameter set.\(^{11}\)

\(^{11}\)Note that adjusting the limits of the integration affects the accuracy of the solutions: not all results possess the same accuracy (with $\lesssim 50\%$ variation). This was taken into rough account, though, as we shall see the phase diagram production method usually introduced much larger uncertainties than the intrinsic numerical errors, which are generally quite small.
A.6. PHASE DIAGRAM CONSTRUCTION

Figure A.6: (a) Convergence of our salt expulsion profile on the Poisson–Boltzmann case, as $\epsilon_2$ is made identical to $\epsilon_1$. (b) Comparison of our code (open circles) when $\epsilon_2 = \epsilon_1$ with Maple (solid line) over a wider range of $H$. The two independent methods agree well. The above curves were obtained using the same parameters as in Table 5.1 except here $\sigma = 0.15 \text{enm}^{-2}$, $c_s^0 = 0.01 \text{M (}\lambda = 30 \text{Å)}$, $\chi = 0.3$, $\delta = 40 \text{Å}$. N.B.: The missing labels on the figures: $c_s$ (vertical) and $D/\lambda$ horizontal.
• The polymer content of the phase $\phi_p$ is changed using the control parameter $\phi'$. The resulting “phase determining” quantities (net pressure $\Pi_{net}$ and polymer content $\phi_p$) are plotted for different values of $\phi'$.

• The entire procedure is repeated for the numerics of the uncoupled model. Here the surface potential range and limit adjustment is easier, since the coupled case can be used as a benchmark.

### A.6.2 Phase Diagrams

In Chapters 5 and 6 we saw how the osmotic interaction between charged lamel-laee indicates two possible types of phase behaviour: one bound lamellar phase coexisting with a reservoir solution ($\Pi_{net}^* = 0$) and two bound lamellar phases of different spacing coexisting with each other ($\Pi_{net}^* > 0$). The determination of coexistence is slightly different for the two cases, as we shall describe in the following. The first step is to identify what kind of equilibrium we are “observing”. The osmotic pressure curve is usually sufficient to tell, but for ambiguous cases, we can use free energy density vs. lamellar volume fraction or lamellar chemical potential vs. pressure as tools for distinguishing the behaviour (see Chapter 6).

$L_\alpha - L_\alpha$ equilibria

• The equal area construction was performed on the osmotic pressure curve for each of the curves obtained as described above (Fig. A.8c). The horizontal line defining the equilibrium pressure and equal areas was obtained “by eye” judgement using moving crosshair ruler of the graphing software Gnuplot up and down until we were satisfied that areas were equal. Where the chemical potential was found with sufficient accuracy (see Section A.4.2), plotting the chemical potential versus the osmotic pressure and looking for the characteristic self–intersection shown in Fig. A.7 provided with an alternative estimate of the area equalities. We found this to be useful for
large areas, but in most other cases the "by eye" technique proved more accurate.

- An uncertainty was associated with the equal area estimation yielding a corresponding uncertainty in the equilibrium pressure (Fig. A.8c).

- The values of the lamellar separations and their uncertainties were found from the intersection between the $\Pi^* \pm \Delta \Pi^*$ lines and the osmotic pressure curve (Fig. A.8c). These were noted down and converted into bilayer volume fractions.

- The uncertainty in the separations had two contributions: the numerical uncertainty mentioned in Section A.4.2 and that introduced by the "by eye" method. Usually the latter was dominant (see Fig. A.8c), but when our method was accurate enough, the numerical uncerainty $\Delta H \sim 2l$ was used as the uncertainty for the equilibrium separations.

- From the separations and their uncertainties, the corresponding equilibrium polymer and salt concetrations and uncertainties were obtained, also by intersection (Fig. A.8a).

$L_\alpha - L_1$ Equilibria

- Here no equal are construction is necessary, the equilibrium pressure is zero (for the reasons explained in Chapter 6), and only one bound phase exists in equilibrium with a solution of polymers and salt (the reservoir).

- The equilibrium lamellar separation is found by looking for the separation at which the pressure intersects the zero axis, the uncertainties are found as explained for the $L_\alpha - L_\alpha$ case (Fig. A.9c). The coexisting phase is approximated as one of infinite separation (null bilayer volume fraction) as explained in Chapter 6.
Figure A.7: The equilibrium pressure $\Pi^*$ found from the self intersection of the chemical potential plotted against osmotic pressure (parametric plot).

- The equilibrium polymer and salt concentrations and uncertainties were also found by intersection as for the $L_\alpha - L_\alpha$ case. The coexisting phase has the reservoir polymer and salt concentration. In the case shown in Fig. A.9a, the bound lamellar phase contains no polymer, so we show only the intersection construction for the salt.

A.7 Improvements

We are aware of the limitations of the custom methods used to generate our numerics and phase diagrams. The method of phase diagram generation, in particular, is not very efficient. Were we given a chance to do it all again, we would probably use conventional methods for the solution of our differential equations and save our “programming creativity” for the development of an automated implementation of the method used in the phase diagram construction.
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