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Double Layer Forces: the Role of Molecular Solvents

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LUND UNIVERSITY

Doctoral Thesis

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Double Layer Forces: the Role of Molecular Solvents

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Abstract

The dielectric continuum model has rightfully been and continues to be a major workhorse for theory and modelling in Surface and Colloid Chemistry. Due to the implicit description of water, entering only as a scaling constant for charge-charge interactions, one would not expect it to work for short distances. However, considerable evidence has been accumulated over the years which shows that this is not the case, and the dielectric continuum model gives a reasonable description sometimes on lengthscales which approach the size of a water molecule!

A first part of this thesis concerns theoretical modeling of the salt dependent water uptake of a complex between DNA and CTA (hexadecyltrimethylammonium). The electrostatic component of the free energy was treated at the Poisson-Boltzmann level. Despite the demanding conditions, with high electric fields, low water content and complex geometry, the dielectric description of water works. The agreement between theory and experiment is quantitative.

To try to understand why the primitive model is working under such conditions, double layer forces with an explicit description of the solvent have been studied through Monte Carlo simulations. A simple and previously well-characterized system of two infinite, like-charged plates with only neutralizing counterions was chosen. The solvent was treated as Lennard-Jones dipoles (Stockmayer fluid) and, for comparison, also at the primitive model level. The forces between like-charged plates in the primitive model agree qualitatively with the molecular solvent ones and the implicit solvent gives a reasonable description of the dielectric screening. As expected, the molecular solvent introduces extra effects, namely packing. The phenomenon of ion-ion correlation attraction, i.e., the attraction of the two like-charged plates, is also reproduced in a molecular solvent. One of the studies includes an analysis of the regime between the dielectric continuum model and the full explicit molecular solvent. This is done by progressively reducing the size of the molecular solvent, doubling its number density, and keeping the dielectric properties constant.

The comparison between the two solvent models requires being able to calculate the dielectric constant for a general dipolar fluid. A simulation methodology has also been developed and tested for this purpose.

Key words: Dielectric continuum model; thermodynamic modeling; molecular solvent; Stockmayer fluid; electrical double layer; Monte Carlo simulations; ion-ion correlations; pressure curves; interaction free energy; packing effects

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List of Papers

This thesis is based on the following papers, which will be referred to in the text by their Roman numerals. The papers are appended at the end of the thesis.

 I Electrostatic attraction between DNA and a cationic surfactant aggregate. The screening effect of salt.
   Cecilia Leal, Elham Moniri, Luís Pegado and Håkan Wennerström
   J. Phys. Chem. B 111 5999-6005. **2007**

 II Ion-ion correlation attraction in a molecular solvent.
   Luís Pegado, Bo Jönsson and Håkan Wennerström
   J. Chem. Phys. 129 Article Number: 184503. **2008**

 III Like-charge attraction in a slit system: pressure components for the primitive model and molecular solvent simulations.
   Luís Pegado, Bo Jönsson and Håkan Wennerström
   J. Phys.: Condens. Matter 20 Article Number: 494235. **2008**

 IV The transition from a molecular to a continuum solvent in electrical double layers showing ion-ion correlation attraction.
   Luís Pegado, Bo Jönsson and Håkan Wennerström
   Manuscript

 V Determining the Dielectric Permittivity of Dipolar Fluids in a Slit Simulation.
   Luís Pegado and Bo Jönsson
   Manuscript

List of Contributions

I   I performed the theoretical part of the study and took part in the writing of the paper.

II   I performed the study and was responsible for writing the paper.

III   I performed the study and was responsible for writing the paper.

IV   I performed the study and was responsible for writing the paper.

V   I performed the study and took part in the writing of the paper.

Other Papers not included in this Thesis

1.   The ozone ring closure as a test for multi-state multi-configurational second order perturbation theory (MS-CASPT2).
Luca De Vico, Luís Pegado, Jimmy Heimdal, Pär Söderhjelm and Björn Olof Roos.
Chem. Phys. Lett. 461 136-141. **2008**

2.   Influence of environmental conditions on the interfacial organization of fengycin, a bioactive lipopeptide produced by *Bacillus Subtilis*.
Marc Eeman, Luís Pegado, Yves F. Dufrêne, Michel Paquot and Magali Deleu.
J. Coll. Interface Sci. 329 253-264. **2009**

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My line between personal and scientific/professional (however you want to call it, but to me it is great fun!) life is thin. There are some people who cross it with me back and forth. From long before my day one I have been the careful and loving plan of my mother, for whom no sacrifice for me, big or small, one-time or daily, was big enough. We are so much alike in our will to change the world, and I hope I never loose that. Wanting to change the world doesn't always mean understanding it. That understanding is true wisdom and comes through my father. He puts things in perspective, when judgement goes astray, and helps me to come back to what really matters. I could less and less do without his clean view on life, and the ballance he provides is no less important than all the rest. I am very much like my mother (and proudly so) but every day I try to be more (also) like my father. Thank you both for doing all for me just because I ask you to, even if you don't always understand why, and that is true unconditional love.

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Contents

Chapter 1

Introduction

Any (good) book in Surface and Colloid Chemistry[1–4] will tell you how important electrostatic interactions are. Charged entities are ubiquitous in nature, and the forces between them control the behaviour of systems in areas as mundane as foods and detergents, as technologically important as materials science and as vital as the life sciences. Current reviews and workshops continue to stress this issue[5,6], and it is a safe statement to say that studying and understanding electrostatic interactions is of great scientific and practical relevance.

The same kind of references will also tell you that the classical description of charge-charge interactions in condensed media, of which water plays a central role, is based on the so-called dielectric continuum model. In this model the interaction between two charges q_i and q_j in a medium, $\omega_{q_i q_j}^{med.}$, is just the interaction in vacuum (i.e., Coulomb's law[7]), scaled down by a constant:

$$\omega_{q_i q_j}^{med.} = \frac{U_{q_i q_j}^{vac.}}{\epsilon_r} = \frac{1}{4\pi\epsilon_0\epsilon_r}\frac{q_i\, q_j}{r_{ij}} \tag{1.1}$$

where r_{ij} is the distance between the two charges and ϵ_0 is the permittivity of vacuum. The scaling factor is the well-know dielectric constant of the medium, ϵ_r, and for water it is around 80.

Replacing a complex reality such as a solvent, with all its molecules and degrees of freedom, by a single number, ϵ_r, is obviously a huge simplification, and this has afforded and still affords considerable progress in our understanding of electrostatic phenomena in liquid media. Such a description enters the picture both in the DLVO theory of colloidal stability[8,9], through the Poisson-Boltzmann (PB) equation, as in general in computer simulations or analytical theories where the charge-charge potential is given by Equation 1.1. In computer simulations Equation 1.1

is known as the Primitive Model (PM) (see, e.g.[10] , for a review with examples of its use), a nomenclature which I will use interchangeably with the more general dielectric continuum model. It is evident that replacing the treatment of all solvent molecules explicitly in a simulation by an implicit solvent, as in Equation 1.1, can reduce the computational effort by orders of magnitude, and allow the study of much larger systems.

Equation 1.1 is macroscopic in essence, being derived for bulk conditions, where the separation r_{ij} between the charges is large. As we shorten the separation between the charges, we would expect this model at some point to break down, and that we would need to start considering the solvent explicitly, rather than implicitly. However, considerable evidence has been accumulated over the past decades of a surprisingly good agreement between experiment and theoretical efforts developed using the dielectric continuum model, in particular down to length scales of a few molecular diameters. Examples include properties as diverse as activity coefficients in (concentrated) sea water solutions[11,12] , phase behaviour in surfactant systems in lamellar phases[13–15] and even in other geometries[16] , the cohesion and setting in cement[17–22] and forces between mica surfaces in electrolyte solutions[23,24] .

The broader context of this thesis is then the central question of why the primitive model is working under conditions for which we would not expect it to work. The particular problem one chose to deal with is the interaction between two (planar) electrical double layers, i.e., two charged surfaces and their associated counterions. This is a classical system in Surface and Colloid Chemistry[1–4,9] , and has been extensively studied over the years both experimentally and theoretically. The focus is on the force between these charged objects, which is a fundamental property of the system, determining its conditions of stability. Using computer simulations the double layer forces (at short separations) in an explicit molecular solvent have been studied, and one investigated how the corresponding primitive model picture conforms to the explicit solvent situation. One specific test was the reproduction, in a molecular solvent, of the ion-ion correlation attraction effect[25] , which is already very well documented in the PM.

The original scientific contributions are made up by the research articles appended at the end of this thesis summary. In the context of this thesis Paper I is seen mostly as yet another example of the success of the dielectric continuum model, under conditions which should challenge its validity. Paper V and the calculation of the dielectric constant of general dipolar fluids comes as a requisite for the comparison between primitive

model and corresponding molecular solvent results, for sufficiently high ϵ_r. The ambition of this summary is to set the stage for a better understanding of the papers. One clear goal is to relate the work performed here with molecular solvents to the corresponding Poisson-Boltzmann and PM pictures, which are well established in the field. This should allow the reader to understand the approximations these possibly more familiar theories introduce, and how the work here builds up on that. I present some further details of the models, make more general thermodynamic considerations and give some gist of the main method used (Monte-Carlo simulations). At no point is the intention to be extensive, nor many times fully rigorous, but rather to highlight some important aspects not covered in the papers, focusing on the underlying physics, rather than on mathematical or formal aspects. The remaining sections of this introduction intend to give the reader some insight into how the dielectric continuum model comes about, as well as on some of its important implications.

1.1 On the origin of ϵ_r in the primitive model

A central piece in classical electrostatics is Poisson's equation[7] ,

$$\nabla^2 \Phi(x, y, z) = -\frac{\rho(x, y, z)}{\epsilon_0} \tag{1.2}$$

which relates a charge distribution ρ in vacuum with the electrostatic potential Φ it creates at a point in space of coordinates (x, y, z). The Laplace operator ∇^2 stands for the partial second derivatives of the function with respect to the spacial coordinates, i.e., $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$. In the simplest case where the charge distribution is a single point charge q located at point i in space (of coordinates (x_i, y_i, z_i)) the solution for the potential at a point j is[7, 26]

$$\Phi_{q_i}(x_j, y_j, z_j)^{vac.} = \frac{1}{4\pi\epsilon_0} \frac{q_i}{r_{ij}} \tag{1.3}$$

with $r_{ij} = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}$, i.e., the distance between points i and j. If another point charge is located at point j one immediately obtains Coulomb's law for the potential energy of interaction between both charges in vacuum:

$$U_{q_i q_j}^{vac.} = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} \tag{1.4}$$

How do we now get the (average) interaction between two charges in a medium (or solvent) of dielectric constant ϵ_r, avoiding having to consider all charge-solvent and solvent-solvent interactions explicitly? Let's assume our solvent is composed of particles which have a permanent dipole moment $\boldsymbol{\mu}$ (throughout the thesis summary bold will be used for vector quantities). The treatment can be generalized for higher order electric moments (quadrupoles, etc.), but the dipolar only case is both instructive and the one of relevance for this thesis. The sum of the dipole moments of all the solvent molecules in a given volume V divided by that same volume, i.e., the dipole moment density, is another important quantity called the electric polarization $\mathbf{P}$:

$$\mathbf{P}(x,y,z) = \left\langle \frac{\sum_n \boldsymbol{\mu}_n}{V} \right\rangle \tag{1.5}$$

where the brackets denote an average over the different configurations of the system (for which both the dipole orientations and the number of dipoles n in V may vary). Writing $\mathbf{P}$ as a function of (x,y,z) assumes a sufficiently small volume V around (x,y,z). It can be shown[7] that the negative of the divergence of the polarization, $-\nabla \cdot \mathbf{P}$, creates an electrostatic potential at point (x,y,z) in space just like the charge distribution ρ in Equation 1.2 did. We can therefore write Poisson's equation for the case of a charge distribution immersed in a dipolar medium as:

$$\nabla^2 \Phi(x,y,z) = -\frac{\rho_{net}(x,y,z)}{\epsilon_0} + \frac{\nabla \cdot \mathbf{P}(x,y,z)}{\epsilon_0} \tag{1.6}$$

where we have stressed that ρ is the distribution of the net charges, i.e., permanent charges on non charge neutral entities (e.g., ions). The exact meaning of the divergence operator is not important for our purposes here and one should just keep in mind that $\nabla \cdot \mathbf{P}$ accounts for the effects of the non-uniformity of the polarization[7]. Another way of putting it is to say that the polarization only has the character of a net charge at the surface of a volume[1].

To proceed we must introduce a relation between the polarization $\mathbf{P}$ and the electrostatic potential Φ. An electrostatic potential is related to an electric field $\mathbf{E}$ by

$$\mathbf{E}(x,y,z) = -\nabla \Phi(x,y,z) \tag{1.7}$$

i.e., the components of the field in the different directions are the partial derivatives of the potential with respect to the corresponding spacial coordinates (e.g., $E_x = -\frac{\partial \Phi}{\partial x}$). It is more or less intuitive that if we apply

an electric field to a dipolar medium the dipoles will orient themselves (i.e., polarize) in the direction of this field. A possible relation between **P** and **E** is[1,7]

$$\mathbf{P} = \epsilon_0(\epsilon_r - 1)\mathbf{E} = -\epsilon_0(\epsilon_r - 1)\nabla\Phi \tag{1.8}$$

The two main approximations introduced are then that the polarization is always directly proportional to the electric field, regardless of its strength (this is the so-called linear response approximation) and that the medium is isotropic, i.e., a field in one direction polarizes the material only in that direction. See, e.g.[27], for a discussion of the cases when these approximations are not introduced. The medium further is assumed to be uniform, i.e., ϵ_r does not depend on the point in space where one is. Equation 1.8 means that

$$\nabla \cdot \mathbf{P} = -\epsilon_0(\epsilon_r - 1)\nabla \cdot \nabla\Phi = -\epsilon_0(\epsilon_r - 1)\nabla^2\Phi \tag{1.9}$$

and introducing this result in Equation 1.6 we obtain a modified Poisson equation, which reads:

$$\nabla^2\Phi(x, y, z) = -\frac{\rho_{net}(x, y, z)}{\epsilon_0\epsilon_r} \tag{1.10}$$

An electrostatic problem in a medium is then just like the corresponding one in vacuum, provided the fields (or potentials) given by the charges in vacuum are scaled down by ϵ_r. The solution of Equation 1.10 for a single point charge is

$$\Phi_{q_i}(x_j, y_j, z_j)^{med.} = \frac{1}{4\pi\epsilon_0\epsilon_r}\frac{q_i}{r_{ij}} \tag{1.11}$$

from which one immediately obtains Equation 1.1.

Before proceeding one further important remark should be made on nature of $\omega_{q_i q_j}^{med.}$, and on why a different symbol is used for it as compared to $U_{q_i q_j}^{vac.}$. Suppose we have more generally a system of m charges (ions) immersed in n dipoles (as a simple model for water molecules). The total potential energy of the system U_{tot} comprises charge-charge, charge-dipole and dipole-dipole interactions (all in vacuum), and is a function of the spacial coordinates of all the particles, $(\mathbf{r}^m, \mathbf{R}^n)$ ($\mathbf{r}$ is a vector giving the coordinates of one of the charges in the system, and there are m such vectors; similarly for the dipoles). A fairly standard procedure in

Statistical Mechanics is to integrate or average out the degrees of freedom of the particles we are not primarily interested in, to obtain an effective energy function which only depends on the coordinates of the remaining particles[28]:

$$\omega_{eff}(\mathbf{r}^m) = -k_B T \, ln \int exp\left[-\frac{U_{tot}(\mathbf{r}^m, \mathbf{R}^n)}{k_B T}\right] d\,\mathbf{R}^n \qquad (1.12)$$

where k_B is Boltzmann's constant and T the temperature. Equation 1.1 is a particular case of this, for the simple situation of only two charges immersed in a medium. The presence of T on the rhs of Equation 1.12 immediately gives it away: whereas U_{tot} is a pure energy (the same going for $U_{q_i q_j}^{vac.}$), ω_{eff} and $\omega_{q_i q_j}^{med.}$ are actually free energies.

1.2   The link between ϵ_r and molecular properties: an illustration

Equations 1.8 and 1.11 tell us that the dielectric constant of a material is a measure both of how it is affected by an (external) electric field, and also of how this material on its turn affects the fields (or potentials) inside the medium it constitutes. By now it should be no surprise that ϵ_r depends directly on the properties of the molecules the medium is made of. There are elegant analytical theories which make such links, like the Debye and Onsager equations[27], but which are not free from serious defficiencies and/or a limited range of validity/accuracy. A thorough discussion of these issues is given in the literature[27], and will not be taken up here. However, they still give (at least) important insight into the connection between ϵ_r and microscopic or molecular quantities. The Debye equation reads:

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{n}{3\epsilon_0 V}\left(\alpha + \frac{\mu^2}{3k_B T}\right) \qquad (1.13)$$

where n/V is a particle number density, and the equation was written for the case of only one type of particles in the system. Unlike in the treatment of the previous section, the equation was generalized to the case of particles which have a polarizability α, besides the permanent dipole moment (of magnitude μ). We therefore see that ϵ_r grows with the dipole moment and polarizability of the molecules, as well as with the particle number density. This is only logical since μ and α quantify the response

of the molecules to an electric field (the field from a point charge, for example). The first term between brackets on the *rhs* of Equation 1.13 is usually known as the electronic polarizability. It measures how much the electrons in the molecule are displaced with respect to the positive charges, giving rise to induced dipole moments. I will not be concerned with this effect in this thesis. By analogy, $\mu^2/3k_BT$ is usually referred to as the orientation polarizability, quantifying how much the permanent dipoles of the molecules align in an electric field, against the randomizing effect of entropy (T).

1.3   The complicated reality that ϵ_r encloses

The derivation of the primitive model (Equation 1.1) from Poisson's equation in Section 1.1, as well the concept of effective potential in Equation 1.12 already gave an overview of the complex reality a dieletric continuum encloses. To put it short, the primitive model is far from being primitive! The treatment in Section 1.1 uses equations of macroscopic electrostatics, and there is no *a priori* guarantee that these should remain valid for microscopic length scales. The same goes for the approximations introduced in Equation 1.8 (polarization directly proportional to electric field, uniform dielectric medium, ...). These become more and more questionable as the distance between charges gets smaller. For a charged species (let's say a simple ion or a macroion) the electrostatic potential it creates in its vicinity increases as the distance to its center decreases (Equation 1.3). This means that a dipole close to this charge will be more and more aligned with its field as we decrease their distance, and one has the concept of solvation shells. Below a certain distance, for a sufficiently high charge, despite the increase in the field, the dipole is already fully aligned, and **P** is no longer proportional to **E** (one is in a so-called saturation regime; to be more stricly correct one should actually be aware that the saturation regime does not start only when the field is sufficiently high that the dipole is completely aligned with it; the deviation from the linear regime begins for a sufficiently high dipole-field interaction, $\boldsymbol{\mu}\cdot\mathbf{E}$, and for $\boldsymbol{\mu}\cdot\mathbf{E} = k_BT$ one can certainly already expect some deviation in the direct proportionality between **P** and **E**). Even if this is not the most complete view of the solvation environment of a charge, it illustrates one of the possible failures of the continuum theory. In the same line of thought, we can imagine that as two charges come together their solvation environments start overlapping, and in this regime one could think that the average of Equation 1.12 is no longer valid, since

the solvent in the inter-charge space is not merely "tumbling around". A further point is that very simply the number of solvent molecules which fits between two charges is not a continuum, but a discrete number, and for sufficiently short separations this should have an effect on the charge-charge interactions.

As also mentioned before, the primitive model is an effective potential, and the interaction energy there is not a pure energy, rather a free energy. Besides the (unscreened) charge-charge interaction it also encloses the charge-solvent interaction, the change in solvent-solvent interaction due to the presence of the charges as well as the change in solvent entropy. A detailed discussion of this is given in[1], to which the reader is referred, where some direct consequences of these facts are further explored. One particular point to keep in mind is that the dielectric constant (for water) is temperature dependent, which immediately gives the entropy connection.

To conclude, I hope to have given sufficient arguments to why one would think that the primitive model should not work at short length scales (small charge-charge separations). Since the contrary seems to be happening, it is then of fundamental interest (but with many practical implications!) to understand why.

Chapter 2

Implicit solvent in a mean-field picture

The forces between charged objects in solution are central for the understanding of such systems, and the structures adopted are merely a consequence of the underlying interactions. This was recognized long ago and led to what is the cornerstone of the theoretical interpretation of colloidal stability: the DLVO theory[8,9]. It combines a description of electrostatics through the Poisson-Boltzmann equation with van der Waals interactions and is still today a powerful tool in rationalizing many relevant problems in Surface and Colloid Chemistry. The focus of this thesis being on electrostatic forces I will therefore devote the next pages only to the Poisson-Boltzmann component. The general state of affairs can be found in standard textbooks[1–4] and there is a plethora of examples of how successful the Poisson-Boltzmann equation can be in describing charge-charge interactions in dielectric media. Some "classics" include surface forces in electrolyte solutions[29,30], phase behaviour in surfactant systems under a range of conditions (salt contents, aggregate shapes, etc.)[16,31] and electrostatic potentials of binding sites of enzymes[32]. Other examples include the analysis of the forces between macroions for a range of parameters[33], and very recently a direct quantitative comparison between theory and experiment in the case of forces between single pairs of polystyrene beads[34]. My primary interest here is to show how this classical level of description is connected to the the primitive model and finally to the simulations with molecular solvents which are the original contributions of this thesis. Another purpose is to stress the two main approximations which the Poisson-Boltzmann theory introduces. Such background is also suitable for the analysis of Paper I.

Let's suppose we have a solution with small mobile charged species (from now on ions), and which in the cases of interest below is confined between some charged interfaces. The Poisson-Boltzmann equation reads[1,2]:

$$\nabla^2 \Phi(x, y, z) = -\frac{1}{\epsilon_0 \epsilon_r} \sum_i q_i \, c_{i0} \, exp\left(\frac{-q_i \, \Phi(x, y, z)}{k_B T}\right) \qquad (2.1)$$

where the summation is over the different types of ions in solution. In the modified Poisson equation (1.10) the distribution of our net charges can be written as

$$\rho_{net} = \sum_i q_i \, c_i(x, y, z) \qquad (2.2)$$

where $c_i(x, y, z)$ is the concentration of ions i at a certain point in the solution. At equilibrium the concentration profiles obey a Boltzmann distribution:

$$c_i(x, y, z) = c_{i0} \, exp\left(\frac{-q_i \, \Phi(x, y, z)}{k_B T}\right) \qquad (2.3)$$

and we immediately obtain Equation 2.1. c_{i0} is the concentration of ions of species i at a point where the electrostatic potential Φ is zero, normally the bulk.

Besides the assumption of a continuum solvent which comes from the modified Poisson equation (1.10), and which as we will see is common to the primitive model, one introduced a further important approximation. The electrostatic potential Φ is not only the potential from sources external to the solution (like our charged interfaces below), but includes also the mean potential from the mobile charged specied (the ions). The word to keep in mind here is mean, and a so-called mean-field approximation has been made. In the context of Equation 2.1 the ions are no longer seen as individual particles which have different positions in space as a function of time, but rather as a mean electrostatic potential and a mean particle distribution. The reader is referred to[1] for further discussion and to[35] for a formal derivation of Equation 2.1 with a great deal of emphasis on the concept of mean electrostatic potentials. Another derivation of Equation 2.1 is given in[36]. This is instructive in pointing out how the Poisson-Boltzmann approximation implies replacing the two particle distribution functions (for the ions) by a product of one particle distribution functions, i.e., the pair correlation function between the

ions is always constant and equal to one, i.e., the correlations between the ions have been ignored.

The Poisson-Boltzmann equation can now be solved for a variety of problems (boundary conditions) and provide fundamental properties of the systems. Two examples of particular interest for the current thesis follow.

2.1 Double layer forces on the Poisson-Boltzmann level

2.1.1 Two interacting double layers

The model system of greatest interest for us througouht this thesis is that of two infinite like-charged plates of smeared-out surface charge density σ, with their associated counterions only, i.e., two identical, salt-free electrical double layers. The interaction between charged plates is a standard in Surface and Colloid Chemistry textbooks[1–4] . This is a good model to study the behaviour of, e.g., lamellar liquid crystalline phases formed by ionic surfactants[37] or of clay systems[38] , and even the interactions between curved charged surfaces provided the radius of curvature is large enough. The salt-free case is chosen here for simplicity, since the focus is on the solvent effects on charge-charge interactions. The effects of added salt for interacting double layers are important in their own right (e.g.,[39–41]) and would without doubt also be interesting cases to study in molecular solvents. However, the general strategy envisaged for this thesis in what regards double layer forces in molecular solvents was to start with as simple a system as possible and to build up in complexity in small and controlled steps. An illustration of this system is given in Figure 2.1, and the reader is allerted to the fact that for clarity the view depicted is actually the one of the primitive model, with explicit mobile counterions and implicit solvent.

2.1.2 The forces in the mean field

In this thesis I am ultimately interested in the forces between the two charged plates in the system of Figure 2.1 B.) when the solvent is described with explicit molecular detail, rather than implicitly through its dielectric constant only. I therefore start by considering how these forces are described on the Poisson-Boltzmann level to in the next chapter continue through the primitive model until finally reaching the molecular
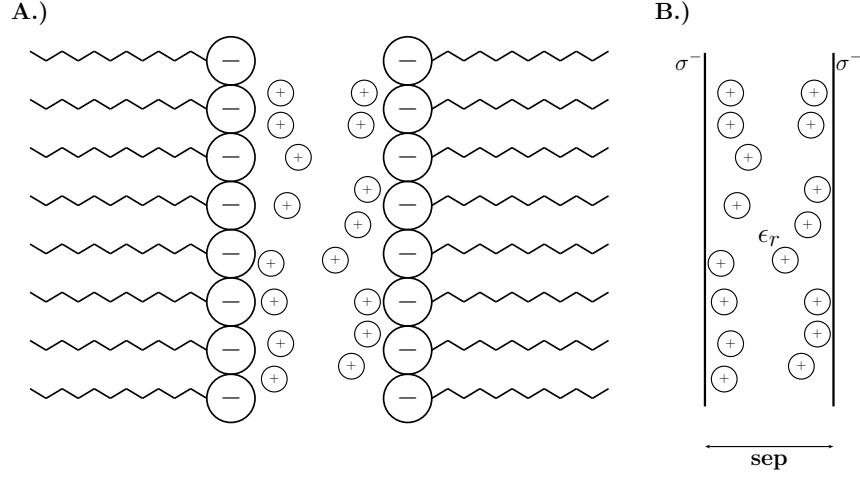
Figure 2.1: A.) A more "realistic" view of a possible experimental realization of the model system in B.): two half-lamellas and the intervening solution in the lamellar phase of an ionic surfactant system. No solvent is displayed for clarity. B.) Two like-charge plates of smeared-out surface charge density with counterions only in the primitive model.

solvent, for which a great deal of results is given in Papers II-IV.

In the framework of the Poisson-Boltzmann equation the force F between two like-charged plates for the salt free case has a particularly simple appearence[42, 43] (see also[37] for some important comments and the relation to the primitive model and[1] for a more pedagogical derivation):

$$\frac{F}{Area} = P_{osm} = k_B T c(mp) \qquad (2.4)$$

where $c(mp)$ is the concentration of counterions at the midplane between the two charged surfaces and one has expressed the result in force per area, i.e., a pressure. The subscript osm stands for osmotic, and is further discussed in subsection 3.2.3. The explicit relation to system properties (ion valency, surface charge density, plate-plate separation, temperature and dielectric constant) need not worry us here. It requires having the solution of the Poisson-Boltzmann equation for the electrostatic potential Φ as a function of z, the coordinate corresponding to the position in the direction perpendicular to the two plates (the potential gives us the counterion concentration at any point in the solution either through its double derivatives, see Equations 1.10 and 2.2, or through Equation 2.3).

Note that for the system of Figure 2.1 B.) the Poisson-Boltzmann equation (2.1) is an ordinary differential equation in z, due to the lateral symmetry in x, y (parallel to the plates), and it has a simple analytical solution for the potential $\Phi(z)$[44]. The ion concentration profile is likewise expressed as a function of z only.

In the case of added salt, i.e., with several charged species in solution, the counterpart of Equation 2.4 just sees $c(mp)$ replaced by $\sum_i c_i(mp)$, where again i are the different ionic species. The solution of the Poisson-Boltzmann equation in the salt case is however much more complicated[39]. A final comment is that in the case of the equilibrium with a bulk electrolyte solution, the relevant quantity to look at is the net force or pressure between the walls, defined as the difference between the pressure for the confined solution (Equation 2.4 extended to several ionic species) and the pressure in the bulk[43]. I do not go further in this since I am not interested in salt cases, but note that the concept of net pressure or force will be important for the molecular solvent simulations (see subsection 3.2.3).

Equation 2.4 tells us that the pressure between the two like-charged surfaces is always positive, i.e., the two plates always repel each other. This is what one would expect intuitively, since like-charges repel each other. However, one should stress that the repulsion between the walls has an entropic character: as the two double layers come closer the ions loose entropy due to the increased confinement. An important consequence of the mean field approximation is that the average field felt by the ions, at the midplane, is zero by symmetry, which means that only the entropic term counts to the free energy. I will return to this when analysing the primitive model in the next chapter. See[1] for a further discussion of energy versus entropy in such systems.

If one wants a view of the slit system in Figure 2.1 B.) on the Poisson-Boltzmann level perhaps the most informative is to draw the electrostatic potential profile between the charged walls, as is done in Figure 2.2. The ion profile has a similar appeerence (with the sign reversed). So in the Poisson-Boltzmann analysis we have lost the individuality of the ions displayed in Figure 2.1, and instead have two smeared-out, uniform (with respect to x, y, i.e, without lateral inhomogeneities) and mean counterion clouds, which are squeezed against each other as the distance between the charged plates is reduced.

We are now ready to put the whole puzzle together and look at the pressure between the plates as a function of their separation. Figure 2.3 compares typical curves for monovalent and divalent counterions. We can
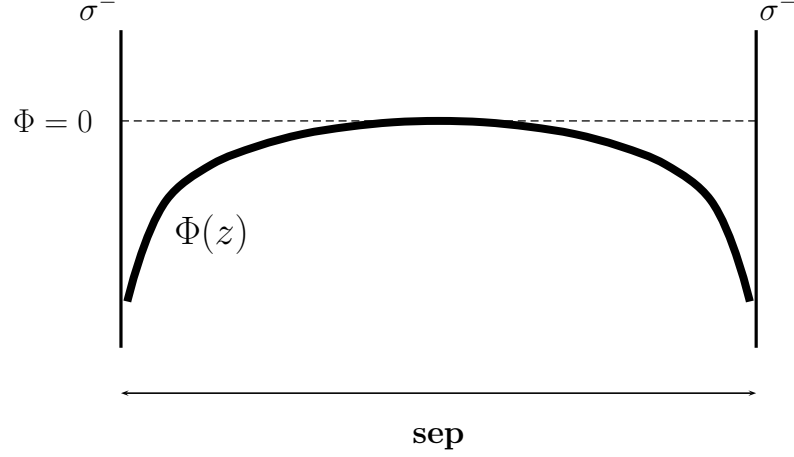
Figure 2.2: Schematic representation of the mean electrostatic potential Φ between two like-charged plates in the Poisson-Bolzmann equation. The situation displayed is that for sufficiently large plate separation. At shorter separations the counterion clouds outside each of the charged surfaces start interacting and the potential is modified (to some approximation it can be taken as the sum of the potentials due to each of the charged plates with their counterions, when isolated).

see that we can increase or decrease the repulsion by tuning the system parameters, and in this case it is somewhat obvious that this repulsion should be reduced for the divalent case, since we have half the number of ions in the slit, as compared to the situation with monovalent counterions. The global picture is always that of an entropic repulsion, though, as noted above. For sufficiently large inter-plate separation this repulsion goes to zero, since the concentration of counterions at the midplane also goes to zero, i.e., the two double layers effectively stop interacting with each other.

2.2   The electrostatic chemical potential for a DNA-CTA system

Another example of the (successful) use of the Poisson-Boltzmann equation is given by the theoretical analysis made in Paper I. This further proves to be one more situation where the implicit description of water through its ϵ_r alone works, when one would not expect it to. In other
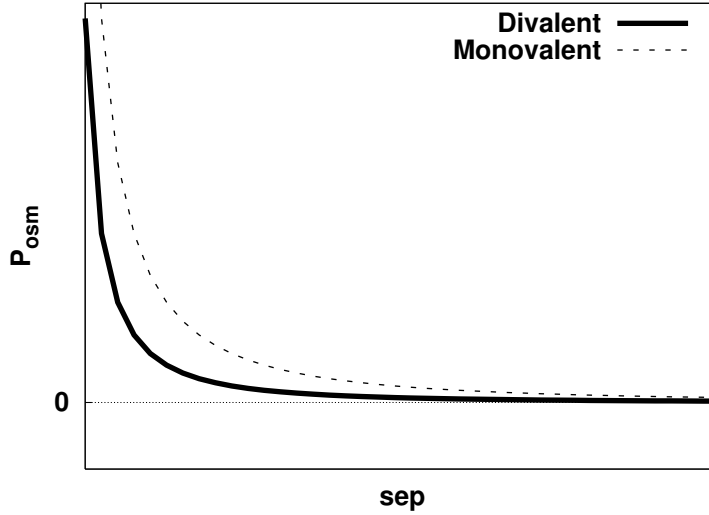
Figure 2.3: Schematic plots for the osmotic pressure as a function of interplate separation for two planar, salt-free double layers at the Poisson-Boltzmann level. Two counterion valencies are compared at the same surface charge density and dielectric constant.

words, in the context of this thesis it is another motivation for the more in-depth analysis of double layer forces performed in Papers II-IV.

Paper I is a combined experimental and theoretical study of the water uptake properties of an aggregate between DNA and the cationic surfactant CTA (hexadecyltrimethylammonium). These form charge-neutral complexes with two-dimensional hexagonal packing, where each CTA cylinder is surrounded by six DNA double helixes (negatively charged). The CTA cylinders are further hexagonally distorted. See Paper I for an illustration of the system. These complexes were well-characterized experimentally, mainly through scattering and calorimetric techniques. Of particular interest for the theoretical analysis are the sorption isotherms, giving the amount of water taken up by the complexes (i.e., their swelling) as a function of water activity (or equivalent chemical potential). When one adds salt to these systems the electrostatic attraction between the negative charges on DNA and the positive charges on CTA is screened,

and the complexes take up more water as compared to what happens in the absence of salt. (Note that this is the only example in this thesis where we considered salt effects, and that in this context screening refers to screening of electrostatic interactions by an electrolyte, as in the concept of the Debye screening length[1–4], not screening by the solvent.)

The quantity to calculate in order to compare with the experimental results was the chemical potential of water for each water content,

$$\nu_{H_2O} = \frac{\partial G_{tot}}{\partial n_{H_2O}} \tag{2.5}$$

where G_{tot} is the total Gibbs free energy of the system, and n_{H_2O} the number of water molecules (note that in this thesis summary ν is used for the chemical potential, rather than the more conventional μ, also used in Paper I, to avoid confusion with the dipole moment). A free energy model for the system was put up, which draws its elements from previous work on phase equilibria in surfactant systems (e.g.[16,31]). Besides the electrostatic free energy, the model further includes a short-range repulsive term and a deformation term. These last two components will not be discussed here, since my focus on this thesis is on electrostatics, and the reader is referred to Paper I for further details on them.

In the definition of the electrostatic component of the chemical potential of water in the complexes, $(\nu_{H_2O})_{el} = \frac{\partial G_{el}}{\partial n_{H_2O}}$, G_{el} is in general the sum of two terms. When no salt is added to the complexes one only has an energy component given by the integral of the electric field squared over the volume of the water regions[7,16]:

$$U_{el} = \frac{1}{2}\epsilon_0\epsilon_r \int (\nabla\Phi)^2 dV \tag{2.6}$$

(see also Equation 1.7)(U is used for the energy to avoid confusion with the electric field; note the different notation in Paper I). It is appropriate to stress that the electrostatic energy for a charge distribution ρ which creates a potential Φ in vacuum is[7] $U_{el}^{vac.} = \frac{1}{2}\epsilon_0 \int (\nabla\Phi)^2 dV$, and Equation 2.6 is linked to it by the same kind of arguments and approximations which connected the Poisson and the modified Poisson equations (1.2 and 1.10) in the Introduction. When we add salt to the system, besides the energetic component we have the entropy of mixing of the ions[16,42]:

$$-T\mathcal{S}_{mix} = k_B T \sum_i \int c_i \left(ln\left(\frac{c_i}{c_0}\right) - 1\right) dV \tag{2.7}$$

where again the integral is over the water domains. c_i are ion concentration profiles just as in Equation 2.3, and c_0 is the concentration of water (~ 0.033 particles/Å^3 or equivalently 55 M).

In Paper I the Poisson-Boltzmann equation (2.1) was solved for the water domains between the DNA and CTA regions, for different amounts of salt added to the system (and for each of these cases for varying water content, obviously), in order to obtain the electrostatic potentials and ion distribution profiles needed in Equations 2.6 and 2.7. Due to the presence of salt, as well as to the complexity of the boundary conditions/geometry, this has to be done using numerical methods (see Paper I for more information, as well as for other details of the model). The main point which I wish to emphasize, and which will be taken up again in the Conclusions, is that the dielectric continuum model was used under quite demanding conditions, which give no *a priori* guarantee of its validity (the water layer separating the charged surfaces - the DNA and CTA domains - is far from a bulk, the geometry is complex, in particular because of the deformation of the CTA cylinders, and the electric fields across the thin aqueous region are high, due to the surface charge densities involved).

A final comment on the DNA-CTA work should be made. In this case one was not strictly interested in pressures, but rather in the chemical potential of water in the complexes, and this was never intended as a direct double layer force study in the sense of Papers II-IV. One should note, however, that the chemical potential of the solvent and the osmotic pressure are directly related quantities, as in the classical osmosis experiment[45]. It is also obvious that the amount of water taken up by the complexes, i.e., their swelling, is related to the forces which hold its components together. Some further comments are made in subsection 3.2.3.

Chapter 3

Beyond the mean field: implicit and explicit solvents

The Poisson-Boltzmann equation can take us a long way. However, there are situations where it can fail even qualitatively. This should not surprise us, since at some point one should pay the price for the approximations which were introduced. Abandoning the mean-field description while still using the dielectric continuum model for the solvent is the subject of classical and well-established work on electrostatic interactions in liquid media, which is therefore taken up first (Section 3.1).

To avoid the mean-field approximation requires treating the charged species explicitly, like it is displayed in Figure 2.1. One possibility is to study the system with computer simulations. As in a reality, the ions will move around, and a given property of interest will be obtained by taking an average over the different configurations adopted.

More than 25 years ago it was shown with Monte Carlo simulations that two like-charged plates with their associated counterions could, under certain conditions, attract at short separations[37]. This effect has since then been confirmed by further Monte Carlo simulations[46,47], as well as using other theoretical approaches, among them integral equation methods[47,48] and density functional theory[49]. Again I stress that this seminal work was performed in the context of the dielectric continuum model (i.e., with implicit solvent), but the interactions between the ions entered the study explicitly through Equation 1.1. The simulations were performed with the so-called primitive model (PM).

This counterintuitive effect of having two large objects of the same

charge which can attract each other is named ion-ion correlation attraction. In the mean field the two like-charged plates in Figure 2.1 effectively do not interact with each other electrostatically. The field across the midplane is zero since on average each half-space (one surface with its counterions) is neutral. This only true on average, though. In reality there are instantaneous deviations from this, which give rise to electric fields from one half-space on the other, and can lead to an attraction. One ion is no longer interacting with a mean potential from all other ions, but rather its position is correlated with those of all the remaining mobile charged species. One way to picture this attraction is to recognize that each ion will create a void of ions of the same charge around itself. For an ion close to the midplane this is equivalent to having a charge of opposite sign on the other half-space, hence the attraction[50]. There is a noticeable analogy between these correlated fluctuations in charge positions leading to an attraction and the disperison interaction, and the reader is referred to[25] for further discussion, where also simple models for the correlation effect are presented.

Ion-ion correlation attraction is important under the conditions of high electrostatic coupling, i.e., high enough counterion valency q, high enough surface charge density σ and/or low enough dielectric constant ϵ_r. This can be put quite elegantly in terms of the dimensionless parameters which characterize the system[37]. Not so long ago the ion-ion correlation phenomenon has been formulated in a field-theoretical framework, in what is known as the strong coupling theory[51,52]. One obtains an analytical solution for the problem of the interplate pressure in a system like in Figure 2.1, valid for strong coupling, the Poisson-Boltzmann result being its counterpart in the weak coupling limit. Again in this context the concept of a coupling parameter Ξ emerges, and one has $\Xi \propto q^3 \sigma / (\epsilon_r T)^2$.

It is important to realize that the ion-ion correlation attraction phenomenon is important under a range of experimentally accessible conditions, and for a big variety of systems. Note that many of the examples given above as successes of the dielectric continuum model are in fact also from systems which display ion-ion correlation attraction. Among them are the swelling of lamellar phases of ionic surfactants, which is much more pronounced with monovalent than with divalent counterions[13–15] and also the swelling of clays or the cohesion properties of cement[17–22,38], where the attraction between like-charged plates with divalent counterions is explaining the underlying phenomena. The direct comparison between force measurements and calculated force curves for mica in the

presence of calcium ions is also worth mentioning in this context[53,54]. All the theoretical efforts mentioned so far in this chapter were undertaken for a system with the same essential elements as that in Figure 2.1, and a big advantage is the connection with experimental studies of actual realizations of the model. This further motivates the choice made in this thesis work regarding the model system to work with. The ion-ion correlation attraction comes as an extra effect which one can seek to reproduce in a theoretical study of double layer forces in a molecular solvent.

Ion-ion correlations also play a role in DNA compaction[55–59], in particular with multivalent ions and in solvents with a dielectric permittivity lower than water. This is again well suported both by theory and experiment, and it is obviously of relevance taking into account the importance of DNA in living organisms. The reader is referred to[25] for further examples of experimental manifestations of ion-ion correlation attraction. Other examples of the phenomenon in different geometries include the attraction between like-charged spheres and cylinders, and a collection of different studies can be found in reference[60]. See, e.g.,[61,62] for the attraction between DNA molecules modelled as cylinders with different levels of "decoration" and[63,64] for the interaction between like-charged macroions, of relevance, e.g., for the behaviour of SDS (sodium dodecyl sulfate) micelles[65].

3.1   Double layer forces in the primitive model

In this section the main physical elements regarding interactions, forces and thermodynamics for the system of Figure 2.1 will be presented, the same being done in Section 3.2 with the molecular solvent model used in this thesis work. Up to here I have used the concepts of force and pressure more or less interchangeably. Of course, the two are trivially related, the advantage with the second being that it is an intensive property. In the context of this chapter, however, a distinction will be made. In our simulation procedure the particles will occupy different positions subject to entropy and interactions. For each of these states or configurations we have forces, for which I will use the symbol F. The symbol P will be reserved for *average* pressures, obtained from the forces for the different configurations with the methods of Chapter 4.

3.1.1   The model and interactions

In the primitive model we already know that the ions interact through Equation 1.1. The total ion-ion energy is therefore

$$U_{qq}^{tot.} = \frac{1}{4\pi\epsilon_0\epsilon_r} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{q_i\, q_j}{r_{ij}} \qquad (3.1)$$

for N ions in our system. In this chapter I will use U for all the energy contributions to the Hamiltonian of the system which enter the simulation protocol. The ions are confined between two infinite walls, each with a smeared-out surface charge density σ. The electrostatic potential from each of them is up to a constant given by

$$\Phi_w = -\frac{\sigma|z|}{2\epsilon_0\epsilon_r} \qquad (3.2)$$

where $|z|$ is the absolute value of the distance from the wall (perpendicular direction). One therefore has a contribution to the total energy of the system given by summing $q_i\Phi_w$ over all ions and doing that for both walls. One of the beauties of the slit system studied in this thesis is that its symmetry affords a great number of simplifications. This will be explored a bit more in Section 4.3 but the full details are outside the goal of this summary (see, for example, Paper II). The potential at a point between both walls when separated by a distance *sep* is

$$-\frac{\sigma|z|}{2\epsilon_0\epsilon_r} - \frac{\sigma|sep-z|}{2\epsilon_0\epsilon_r} = -\frac{\sigma\, sep}{2\epsilon_0\epsilon_r} \qquad (3.3)$$

i.e., a constant. This means that the corresponding ion-wall energy will therefore not influence our Monte Carlo procedure, which is only sensitive to energy differences. More importantly, one should realize that in such a system the ions individually do not have a preference for any position between the walls and, for example, if they accumulate at the charged plates it is due to ion-ion repulsion, rather than to an ion-wall attraction.

In principle, provided our walls were impenetrable, so that the ions would not move pass them, we could simulate a system with the potentials already presented. This would mean we would be using point ions (i.e., ions without a size), as was done in classical work on double-layer forces[37] . This is fine in the counterion only case, since on electrostatic grounds alone each ion creates a volume around itself which essentially no other ion occupies (the so-called Coulomb hole). In a general case where one has attractive electrostatic interactions, like in the next section, it

is no longer possible to use the point ion approach, since the particles would collapse onto each other. For a direct comparison between the results of primitive model and molecular solvent simulations it is therefore desirable to use the same treatment of molecular size throughout. The simplest possibility is to have the ions represented as hard spheres (like in Figure 2.1). The potential is zero outside the sphere and infinite inside, so that nothing can penetrate, regardless of electrostatics. For technical reasons connected with the pressure evaluation, in this work a Lennard-Jones potential was used instead (i.e., soft spheres):

$$U_{qq\,LJ}^{tot.} = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} 4\varepsilon \left[\left(\frac{\varsigma}{r_{ij}} \right)^{12} - \left(\frac{\varsigma}{r_{ij}} \right)^{6} \right] \tag{3.4}$$

where ς is the molecular size (the particle diameter) and ε the value of the maximum attractive interaction between both particles (at a center-to-center distance of $\sqrt[6]{2}\varsigma$). For a low ε such a potential can for the purpose be considered as sufficiently close to a hard sphere potential. In the same line of thought, instead of seeing hard, impenetrable walls, the ions interact with two Lennard-Jones surfaces:

$$U_{qw\,LJ}^{tot.} = \sum_{i=1}^{N} \left(\frac{A}{z_i^9} - \frac{B}{z_i^3} \right) \tag{3.5}$$

(a similar sum has to be done for the opposite wall). The A and B parameters are obtained assuming that the walls are composed of the same Lennard-Jones particles as the solution, at cubic close packing (packing density=0.74). For a single ion:

$$
\begin{aligned}
U_{q_i\,w\,LJ} \;=\; & \varrho\,4\varepsilon \int_0^{2\pi} \int_0^{\infty} \int_0^{\infty} \left(\frac{\varsigma}{\sqrt{\delta^2 + (z_i + \zeta)^2}} \right)^{12} \\
& - \left(\frac{\varsigma}{\sqrt{\delta^2 + (z_i + \zeta)^2}} \right)^{6} \delta\,d\delta\,d\zeta\,d\varphi
\end{aligned}
\tag{3.6}
$$

where the integration is performed in cylindrical coordinates (see Paper II for the solution for A and B). ϱ is the density, $0.74/(\frac{4}{3}\pi(\frac{\varsigma}{2})^3)$.

3.1.2   The forces

To calculate the average pressure between the charged walls is an application of the virial theorem[66, 67]. At equilibrium, the pressure in the

direction perpendicular to the plates is the same throughout the system, for a certain surface-surface separation. One can place an imaginary plane (parallel to the two charged plates) at any position between them, and calculate the forces across that plane. Two locations are commonly chosen for the pressure calculation: the midplane between the walls and one of the walls[37, 40, 43, 46].

3.1.2.1   At the midplane

At the midplane the pressure is a sum of three terms:

$$P_{osm} = k_B T c(mp) + P_{el} + P_{LJ} \qquad (3.7)$$

The first term already appeared in the corresponding Poisson-Boltzmann expression (Equation 2.4), and is normally known as the ideal entropic term. The remaining two correspond to the sum of all electrostatic and Lennard-Jones forces between entities (particles and walls) on opposite sides of the midplane. Again I stress that what is represented above are averages of forces (divided by an area) over different configurations of the system, obtained through Monte Carlo simulations.

The average electrostatic force exerted by one half-space (ions plus wall) on the wall on the other half-space is zero by electroneutrality[46], a further simplification for the slit system. One can easily arrive at this result by recognizing from Equation 3.2 that the component of the field in the z direction (perpendicular to the plate) from an infinite charged surface is

$$E_w^z = \frac{\sigma}{2\epsilon_0 \epsilon_r} \qquad (3.8)$$

i.e., independent of distance. The force from all the charge in one half-space on the wall in the opposite half-space, a product of the type charge×field, is therefore zero, since the total charge of one half space (ions plus wall) is on average zero. The force on the ions in one half-space by the ions and wall in the opposite half-space is not zero, though. The total ion-ion electrostatic force in the z direction is, for a certain configuration of the system:

$$F_{qq}^{tot.,z} = \frac{1}{4\pi\epsilon_0\epsilon_r} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{q_i q_j |r_{ij}^z|}{r_{ij}^3} \qquad ; \qquad (z_i < 0 \, ; z_j > 0) \quad (3.9)$$

where r_{ij}^z is the z component of the vector connecting i and j. The condition after the equation means that one only sums forces between particles on opposite sides of the midplane, which is located at $z = 0$ in the coordinate system chosen (i.e., one sums when $(z_i < 0 \, ; z_j > 0)$ and vice-versa). Equation 3.9 can be obtained from Equation 3.1 by the relation $\mathbf{F} = -\nabla U$. Remembering that the force will be a product of charge×field, it is easy to see from Equation 3.8 that the total force exerted by the wall in one half space on all the ions in the other half-space averages to a constant value, when taken per unit area (i.e., a constant pressure):

$$
\begin{aligned}
\frac{\left\langle F_{qw}^{tot.,z} \right\rangle}{Area} &= \frac{1}{Area} \left\langle \sum_{i=1}^{N} q_i \frac{\sigma}{2\epsilon_0 \epsilon_r} \right\rangle \qquad ; \qquad (z_i < 0 \, ; z_w > 0) \\
&= \frac{Nq}{2Area} \frac{\sigma}{2\epsilon_0 \epsilon_r} = -\frac{\sigma^2}{2\epsilon_0 \epsilon_r}
\end{aligned}
\tag{3.10}
$$

since on average one has half of the (like-charged) ions in one half-space, and by electroneutrality that total ionic charge divided by area must be $-\sigma$. We will encounter the $-\sigma^2/(2\epsilon_0 \epsilon_r)$ term again just below. Due to some specificities of the simulation procedure in what regards the treatment of long-range electrostatic interactions, Equation 3.10 is in practice not directly used for the pressure evaluation at the midplane, being cancelled by another term. See more details in Section 4.3 and in Paper II.

In a very similar way, using $\mathbf{F} = -\nabla U$ one can obtain the formulas needed in the calculation of P_{LJ} from Equations 3.4 and 3.5. Again one must remember to count only forces between entities (particles and walls) on opposite sides of the midplane. The Lennard-Jones force exerted by one wall on the other has not normally been considered in this thesis work. See a comment on it in Paper II.

A note on hard spheres

Had one used a hard sphere potential to represent excluded volume effects, rather than Equation 3.4 (and also having hard instead of soft walls), and Equation 3.7 would read instead:

$$
P_{osm} = k_B T c(mp) + P_{el} + P_{col}
\tag{3.11}
$$

The Lennard-Jones term is replaced by a component corresponding to collisional integrals between the hard spheres across the midplane. Details can be found in[46], but it suffices to say that these are more cumbersome to evaluate than the direct calculation of a Lennard-Jones force. This would become a bigger drawback with more particles in the system, i.e., in the molecular solvent cases.

3.1.2.2   At the walls

If one evaluates Equation 3.11 at one of the charged walls, the collisional term will disappear, since there are no particle-particle contacts across that plane, and the ideal entropic term becomes $k_B T c(walls)$, i.e., the concentration of ions at the walls. The electrostatic term now corresponds to the forces on that wall from all the ions and the remaining wall. From Equation 3.8, and with similar arguments as above, we can see that $P_{el} = -\sigma^2/(2\epsilon_0\epsilon_r)$ (the wall-wall electrostatic pressure cancels with the pressure on the wall from half of the ions, and one gets the term corresponding to the remaining charges). The total pressure is then

$$P_{osm} = k_B T c(walls) - \frac{\sigma^2}{2\epsilon_0\epsilon_r} \tag{3.12}$$

where the electrostatic component is usually known as the Maxwell term. The reason for having started with the hard spheres version of the pressure equation here is that the above result can be given a more formal framework than the "virial-like derivation" made here, and it is the classical contact value theorem[43,68].

     With Lennard-Jones particles the concentration of ions at the walls is zero, but one instead has a Lennard-Jones force from all the particles in the system:

$$P_{osm} = P_{LJ} - \frac{\sigma^2}{2\epsilon_0\epsilon_r} \tag{3.13}$$

where P_{LJ} is an average over different configurations of the system. One should not forget the difference with respect to the corresponding term in Equation 3.7 (only Lennard-Jones forces from all the particles on one wall, again using the gradient of Equation 3.5, rather than particle-particle and particle-wall forces across the midplane). Equation 3.13 can be obtained from Equation 3.7 with the same kind of reasoning that linked the two corresponding hard spheres equations (wall and midplane). Similarly to before, it turns out more convenient to use an equation like 3.13 than 3.12. The former relies on a direct computation from

force formulas, whereas the latter requires evaluating the concentration at the walls by extrapolation of the (in that region rapidly varying) ion concentration profiles. Note that the concentration profiles close to the midplane are much more well-behaved, and this is not a problem in Equation 3.7 (the concentration profile will have the same qualitative look as in Figure 2.2, with the sign changed, as indicated when discussing the Poisson-Boltzmann theory).

3.1.2.3 Comparison to the mean-field

Now suppose we have already obtained proper averages for the quantities needed in either Equation 3.7 or 3.13 through, for example, Monte Carlo simulations. The primitive model picture corresponding to the mean-field, Poisson-Boltzmann solution in Figure 2.3 is schematically displayed in Figure 3.1. The most striking effect is the qualitative difference between the results for divalent counterions. For monovalent counterions we have quantitative deviations (see, e.g.,[37]), but we still get the traditional double layer repulsion. However, for divalent counterions, at the surface charge density and dielectric constant chosen, the electrostatic coupling (remember Ξ) is sufficiently high that the repulsion is turned into an attraction, due to ion-ion correlations. The coupling parameter Ξ also tells us that we could again turn the attraction into a repulsion by decreasing σ or increasing ϵ_r (see Paper II).

Had we done a simulation with point ions instead then the P_{LJ} term in Equation 3.7 would disappear (but we would still get the same general picture as in Figure 3.1[37]). Comparing Equations 2.4 and 3.7, there will be differences in the $c(mp)$ terms between primitive model and Poisson-Boltzmann solutions. Anyway, this component can only give an (entropic) repulsive contribution to the pressure, and the fact that we can get a correlation attraction at all comes from the P_{el} term (zero in the mean-field).

An important conclusion is that the correlation attraction depends on a balance between entropic repulsion and electrostatic attraction, and one can enter (or leave) the correlation regime by changing $c(mp)$ or P_{el}. An obvious way of changing the ideal entropic term is by changing the counterion valency, as was done in the current example, and one of changing P_{el} is changing ϵ_r. In fact, even though we need the negative P_{el} term to get the correlation attraction, it is important to realize that in the example of Figure 3.1 the change from correlation attraction to double-layer repulsion came about essentially from an increase
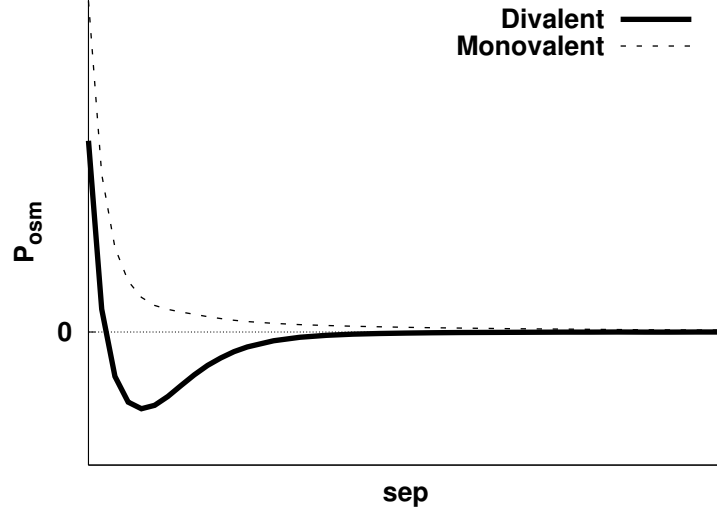
Figure 3.1: As in Figure 2.3 but for primitive model simulations.

in $c(mp)$ for monovalent counterions, not from the (small) change in P_{el} between the two counterion valencies (note: the P_{LJ} term increases the curve separation even further, see Paper III). Paper III gives several examples of what happens to the pressure in the system upon changing q, σ and ϵ_r, together with the corresponding pressure components. In the context of this thesis the analysis of the different pressure terms for Equation 3.7, as well as their subcomponents, will turn out as a valuable aid in providing insights into the system behaviour and aiding the comparison between primitive model and molecular solvent results (Papers III and IV especially). A more "mathematical" view of the correlation attraction phenomenon is given in Section 4.3, also using pressure (sub-) components (through the P_{el} term), in a more technical framework.

3.1.3   Thermodynamic framework

The thermodynamic state of the system in Figure 2.1 is specified by the independent variables (N, V, T), N being the number of ions for a (constant) system volume V, and T the temperature. These are the

same constraints which will later on be interesting to us since they are also imposed on the Monte Carlo simulations in the primitive model. In this context one works in the so-called Canonical ensemble.

The relevant thermodynamic potential (minimized at equilibrium[69]) is the Helmoltz free energy A. From basic Thermodynamics[45], its differential is:

$$dA = -PdV - \mathcal{S}dT + \nu_{ions}dN_{ions} \qquad (3.14)$$

where P is pressure, $\mathcal{S}$ entropy and ν chemical potential. For constant temperature and number of particles we get:

$$P = -\left(\frac{\partial A}{\partial V}\right)_{T,N_{ions}} \qquad (3.15)$$

This expression is useful since it shows that the integral of the pressure with respect to system volume gives a free energy (note that in our slit system the volume change is given by the change in surface-surface separation, at constant surface area). This procedure is used in Papers II and IV when integrating the osmotic pressure curves. See also the follow-up in subsection 3.2.3.

3.2 Double layer forces in a dipolar fluid

We now come to the heart of this thesis work. We have already abandoned the mean-field description of charge-charge interactions and seen the important effects which are captured. A natural follow-up is to go beyond the second important simplification which the Poisson-Boltzmann theory introduced, and the primitive model kept: the dielectric continuum model. This is especially interesting taking into account the puzzling fact that the implicit solvent description seems to be working when we would not expect it to. The situation here is clearly much less developed, and there is certainly a long way to go before we master all the finesses of charge-charge interactions in molecular solvents.

From a more global point of view one should first say that, despite the considerable amount of evidence which substantiates how well-behaved the primitve model is, it is common to find stated in the literature that water outside surfaces behaves very differently from the bulk (e.g.,[70,71]). Just this on its own already tells you that there is certainly a problem out there deserving further attention. Turning to our subject matter more specifically, it can be said that most of the theoretical studies done

for ions and (elaborate, discrete) water models between charged surfaces
have concentrated on structural properties like particle distribution pro-
files, and stayed away from surface forces (e.g.,[72–74]). I note that this is
valid for the subject of double layer interactions in general, and is not
limited to the planar geometry nor to the ion-ion correlation attraction
phenomenon. As of the year 2000 reviews on the topic listed only a few
studies of discrete solvent effects on double layer forces[75], and still to-
day it is recognized that there is a need for even more general work on
electrical double layer properties beyond the primitive model[76].

One very simple molecular solvent which has been used in theoreti-
cal studies of the interaction between like-charged plates is the so-called
SPM (solvent primitive model). Here the charge-charge interactions are
still scaled by the dielectric constant of the medium, like in Equation 1.1,
but one further introduces neutral hard spheres in the system, which are
supposed to account for the effects of solvent granularity, by describing
the size of its molecules. The model looks like that of Figure 1 in Paper
II, but with the arrows corresponding to the dipoles removed. The primi-
tive model picture discussed in the previous section clearly does not come
forward in these studies, either because one finds only (essentially mono-
tonic) repulsive forces between the plates, even for divalent ions[77], or
because the behaviour is dominated by oscillatory profiles due to solvent
packing effects[78,79], being largely insensitive to ion valency. The SPM
has also been used to study the forces between neutral and like-charged
(spherical) colloidal particles[80,81]. The effects of solvent granularity on
the forces are clearly displayed and in some cases (but not in others!)
an agreement with the primitive model solution was found. Besides this
plethora of results, it is important to realize that the SPM treats the
excluded volume effects (the size of the particles) and the electrostatics
on unequal footing, since only the former have been discretized (there
are no solvent dipoles or higher electric moments). This can constitute
an unballanced description.

Molecular solvent effects on forces between like-charged surfaces have
also been introduced at the McMillan-Mayer level, using integral equa-
tion methods. In this case the medium enters the picture through effec-
tive, solvent averaged ion-ion potentials. These are normally written as
the sum of Equation 1.1 with an extra (distance dependent) term, which
accounts for the molecular nature of the solvent. The ion-ion correlation
effect was reproduced, with an attraction between the surfaces for diva-
lent counterions, but one also found a solvent induced attraction when
only monovalent ions were present, a result not given by the PM[82,83].

In general, the results are found to be very sensitive to the potentials used[84]. Note also that the effective ion-ion potentials are obtained from bulk simulations, either at infinite dilution or at finite salt concentration, which neglects the changes which can be introduced for inhomogeneous systems, i.e., ions between two walls.

Solvent models where the particles are represented by spheres with embedded dipoles and even higher order moments have also been considered. One example is a study of the interaction between like-charged macroions in a monovalent electrolyte[85], where it was found that such objects could attract for a given range of parameters. A system of ions and dipoles between planar surfaces has also been considered[86]. Here one has however studied a slit formed by one charged and one uncharged plate, and the focus was on structural information.

Credit should be given to the (simulation) work on forces for ions and water between charged surfaces performed within the context of the physical chemistry of clay systems[87–93]. These studies are in general characterized by using water models more elaborate than the simple dipolar spheres, and in particular for having atomic detail level description of the clay surfaces. Their merit tends to be more centered in addressing important but specific problems (e.g., influence of surface details or chemical identity of counterions on the system properties), and they are therefore outside the scope of this thesis. I stress that the focus here is the general and fundamental question of the influence of the description of the solvent for charge-charge interactions, in this case assessed through studies of such an important property as are double layer forces. A particular interest is how the dielectric continuum model agrees (or not) with a molecular description.

The Poisson-Boltzmann theory can be modified by adding a term to the free energy which accounts for discrete solvent effects on ion-ion interactions. This was also tried in studies of forces between planar like-charged surfaces[94], where a solvent-mediated attraction was found with only monovalent ions in solution. Such an approach has obvious contact points with the McMillan-Mayer level of description, although the formalism here tends to be simpler and one can extract some analytical results. However, one again pays a price for approximations introduced (in particular, as we already know, correlation effects cannot be captured). Even if aimed at a physical understanding of the system, this approach is not really compatible with the level of (molecular) detail envisaged for this thesis work. One should also mention the work done on the fundamental understanding of dielectrics in a slit[95]. This gives you

insight on the inadequacy of a constant ϵ_r in describing the dielectric properties of a confined dipolar liquid, but still does not rule out that Equation 1.1 is a good description for the charge-charge interactions.

Taking the previous paragraphs into account, it was therefore considered that the general problem of charge-charge interactions in dielectric media at short distances was sufficiently complex to be worthy of a thorough and systematic study. The strategy envisaged was to start with a simple, yet relevant, and previously well-characterized model system (i.e., the slit of Figure 2.1) and to progressively increase the complexity of the description, starting at the primitive model level. The first step is to introduce a sufficiently simple (but balanced!) discrete solvent model, and to study surface forces with computer simulations at this level of molecular detail. Different levels of complexity can later on be introduced, like the effects of discrete surface charges, more elaborate solvent models (less symmetry, polarizabilities, etc.). Anyway, this should be done in controlled steps, moving to the next (solvent/surface) model once the previous is mastered. Otherwise one faces the danger of being lost in a jungle of effects, with causes difficult to identify. This will at each stage hopefully contribute to our understanding of why the primitive model is behaving the way it is. This step-wise strategy includes even the interaction parameters used in the simulations, see 4.3.1. One example of its usefulness comes from comparing the work in Paper II with the corresponding systems in Paper IV (the S_0 case). Had one started the studies with the kind of interaction parameters of Paper IV, rather than with thoses of Papers II and III, one would be unaware of the clear-cut comparison with the PM that the dipolar solvent model can afford (Papers II and III). I would also like to stress how instrumental the analysis of different pressure components can be in aiding the interpretation (also in Paper IV).

3.2.1   The model and interactions

The molecular solvent model used throughout this thesis work is a so-called Stockmayer fluid. This consists of a Lennard-Jones sphere with an ideal dipole located at its center. See Figure 1 in Paper II for a pictorial representation. Again, the Lennard-Jones potential was chosen for technical reasons connected to the pressure calculation, and one could have used hard-spheres to model the excluded volume effects as well. A physical dipole is formed by two charges of opposite sign, $-q$ and q, separated by a certain distance l, and its magnitude is $\mu = ql$. One

can reduce the distance l and increase the charges so that μ is constant, and an ideal dipole is the construction one gets in the limit where the two charges coincide[27] ($l \to 0\,; q \to \infty\,; ql = cte = \mu$). I stress that in a dipolar fluid one has discretized the medium both with respect to excluded volume and to electrostatic effects. One can conceive this as a minimal model for, e.g., a water molecule. The dielectric response of the solvent is now a direct consequence of its properties (μ, density), rather than simply a scaling constant (ϵ_r) for the charge-charge interactions, as in the primitive model.

The total electrostatic energy of the system now contains ion-ion, ion-dipole and dipole-dipole interactions. The first are given by Equation 3.1 above, removing the ϵ_r scaling factor (i.e., the traditional Coulomb's law in vacuum). The formulas for the remaining two can be found in standard textbooks[96]. The total ion-(ideal) dipole interaction reads:

$$U_{q\mu}^{tot.} = \frac{1}{4\pi\epsilon_0} \sum_{i=1}^{N_{ions}} \sum_{j=1}^{N_{dip}} q_i \frac{\boldsymbol{\mu}_j \cdot \mathbf{r}_{ij}}{r_{ij}^3} \tag{3.16}$$

where $\boldsymbol{\mu}_j \cdot \mathbf{r}_{ij} = \mu_j^x r_{ij}^x + \mu_j^y r_{ij}^y + \mu_j^z r_{ij}^z$ (scalar product between the dipole moment vector and the vector pointing from dipole j to ion i). For the dipole-dipole interaction:

$$U_{\mu\mu}^{tot.} = \frac{1}{4\pi\epsilon_0} \sum_{i=1}^{N_{dip-1}} \sum_{j=i+1}^{N_{dip}} \frac{\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j}{r_{ij}^3} - \frac{3(\boldsymbol{\mu}_i \cdot \mathbf{r}_{ij})(\boldsymbol{\mu}_j \cdot \mathbf{r}_{ij})}{r_{ij}^5} \tag{3.17}$$

Yet another simplification afforded by the slit system is that the dipole-wall electrostatic interaction is zero. This energy is for each dipole a scalar product between the dipole moment vector and the field from the two walls. A constant potential (Equation 3.3) implies a zero electric field between the walls.

The formulas of Equations 3.4 and 3.5 now have to be extended to include the Lennard-Jones interactions between all ion-dipole and dipole-dipole pairs, as well as the interactions of the dipolar soft spheres with the two Lennard-Jones walls.

A simple and direct manifestation of the molecular size, as well as of the increased density in the molecular solvent case, is given by looking at a concentration profile for dipolar particles alone between uncharged walls. A schematic example is shown in Figure 3.2. Closer to the walls one sees oscillations whose period reflects the molecular diameter, but
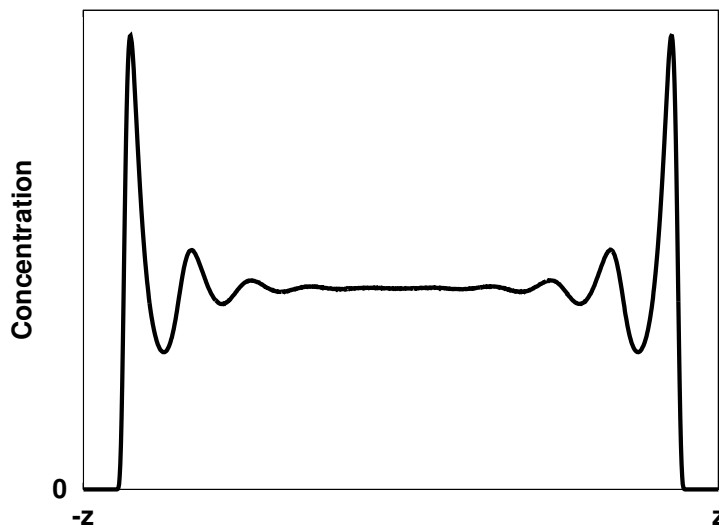
Figure 3.2: Molecular packing effects in a typical concentration profile for Lennard-Jones spheres confined between two walls. The walls are located at $-z$ and z.

as one goes more and more away from the surfaces (into the bulk), this structure is lost. It should be noted that the profile is qualitatively the same for dipolar and neutral Lennard-Jones spheres. Concentration profiles and forces between two neutral walls with a Lennard-Jones fluid in between (no dipoles) can be found in classical work by Snook and van Megen[97–99]. These oscillations will also come into play when one has ions and dipoles between charged surfaces, and will reflect themselves on the pressure curves, as is extensively discussed in Papers II-IV. Note further that something qualitatively similar will also happen if the Lennard-Jones potential is replaced by a hard-sphere one.

3.2.2   The forces

The pressure calculation in the molecular solvent case is done with simple extensions of Equations 3.7 and 3.13. In the case of the evaluation at the midplane, $c(mp)$ is now a sum of ion and dipole concentrations. The P_{el}

term has the same charge-charge components as before (removing the ϵ_r factor), but now has to include the z components of forces between ion-dipole and dipole-dipole pairs (averaged over different configurations of the system), when each of the particles sits on opposite sides of the midplane:

$$P_{el} = \frac{1}{Area} \left(\left\langle F_{qq}^{tot.,z} \right\rangle + \left\langle F_{q\mu}^{tot.,z} \right\rangle + \left\langle F_{\mu\mu}^{tot.,z} \right\rangle \right) \quad ; \quad (z_i < 0 \,; z_j > 0)$$

(3.18)

where the ion-wall term (see Equation 3.10) was ommited for simplicity. The revelant formulas can be obtained from the gradients of Equations 3.16 and 3.17, and are to be found in Paper II. Note that in that context the treatment in Equation 3.18 will carry some further specificities (technicalities) due to the handling of long-range interactions. It should not surprise us at this point that there are no dipole-wall electrostatic forces. A dipole gets a force from an electrical field gradient which, from Equation 3.8, is zero. Finally, one should not forget the forces between Lennard-Jones ion-dipole and dipole-dipole pairs (opposite sides of the midplane) and between soft walls in one half-space and particles on the opposite half-space, which go into the P_{LJ} term.

At the walls the only difference with respect to the primitive model is that the P_{LJ} term now includes also the Lennard-Jones forces from all the dipoles on that wall. In a notation similar to that of Paper II:

$$P_{osm} = LJ_{iw} + LJ_{\mu w} - \frac{\sigma^2}{2\epsilon_0}$$

(3.19)

where the LJ terms represent averages.

The general comparison of primitive model and molecular solvent pressure curves is the main subject matter of this thesis, and the reader is now referred to Papers II-IV.

3.2.3   Thermodynamic framework

A very important point for our slit in the molecular solvent studies (see Figure 1 in Paper II) is that it is an open system with respect to the dipoles. The number of ions and the temperature are always fixed. For a certain plate-plate separation, the (average) number of dipoles between the surfaces is given by their molecular properties (like the dipole moment μ) and by the bulk chemical potential of the fluid. In other words, one is always at equilibrium with a reservoir of bulk liquid, with which

particles are exchanged. Within the context of Statistical Mechanics we then work in the Grand-Canonical ensemble (strictly speaking, we have what is normally referred to as a semi-Grand ensemble, since the system is only open with respect to the dipoles, but not to the ions[28]). The relevant thermodynamic potential is now a Grand-Canonical one, and its differential reads:

$$d\Omega = -PdV - \mathcal{S}dT - N_{dip}d\nu_{dip} + \nu_{ions}dN_{ions} \qquad (3.20)$$

For constant temperature, number of ions and chemical potential of the solvent, ν_{dip}, one obtains:

$$P = -\left(\frac{\partial \Omega}{\partial V}\right)_{T,\nu_{dip},N_{ions}} \qquad (3.21)$$

We can see that we can integrate a pressure curve as a function of plate-plate separation to get a free energy (in the slit case $dV = Area\,dsep$, $Area$ being our constant plate area and sep the variable separation).

The quantity displayed in Papers II-IV is actually a *net* (osmotic) pressure. This is defined as the difference between the pressure in the direction perpendicular to the charged plates for our (confined) system (which is what is covered in the previous subsection on forces, for example), and the bulk pressure of our solvent:

$$P_{osm}^{net} = P_{osm}^{conf} - P_{osm}^{bulk} \qquad (3.22)$$

The actual integration which is performed in Papers II and IV is:

$$\frac{\Omega^{ex}(sep)}{Area} = \int_{sep}^{\infty} P_{osm}^{conf}(z) - P_{osm}^{bulk}\,dz \qquad (3.23)$$

from which we obtain an interaction free energy per unit area, at a certain plate-plate separation. Remember that this happens at constant temperature, number of ions, chemical potential for the solvent and plate area. In Equation 3.23 a term $\Omega^{ex}(\infty)$ has actually been dropped for simplicity, which corresponds to twice the surface free energy of each plate. Strictly speaking, what is reported are differences with respect to this constant value. The quantity in Equation 3.23 has the character of an excess free energy. This can be understood by remembering that for a bulk, one component fluid at constant temperature and chemical potential one has a pure Grand-Canonical energy given by[66]:

$$\Omega = A - N_{dip}\nu_{dip} = -PV \qquad (3.24)$$

where P in this case is the bulk pressure. This perhaps affords a complementary view on the concept of net pressure. Note that in the primitive model the integration performed is also like in the *rhs* of Equation 3.23. However, in this case one has $P_{osm}^{bulk} = 0$ (in the salt-free case!).

Both for forces (pressures) and free energies we then look at net effects referred to a bulk solution (solvent only in this case). What I wish to stress is that changing the bulk we are at equilibrium with also affects the behaviour between the slit, which has obvious analogies with the traditional concept of osmosis and lends meaning to the *osm* superscript used throughout[1].

Chapter 4

Monte Carlo simulations

In a real system atoms and molecules are moving around and occupy different positions as a function of time. An experimental measurement of a property of that system is an average over a (possibly very small) time interval of its fluctuating, instantaneous values. The direct study of the time evolution of a system in a computer with the calculation of relevant properties belongs to the realm of Molecular Dynamics simulations, which were not used in this thesis work and will not be covered here. In this chapter a small overview of the relevant Monte Carlo methods and of how they are used to calculate the (average) properties of the slit systems I am interested in is given, with particular emphasis on the pressure between the charged plates. Monte Carlo (as well as Molecular Dynamics) are nowadays well-established simulation techniques, and the reader is referred to standard textbooks for extensive details[67, 100, 101].

In a Monte Carlo simulation one replaces the computation of time averages by ensemble averages, which is allowed due to the so-called ergodic hypothesis. Instead of studying the time evolution of a single system, one uses a collection of replicas of the system, which is called an ensemble[28]. These replicas are in the same thermodynamic state, specified, e.g., by a constant number of particles, volume and temperature, but differ microscopically (the particles occupy different positions and we have different configurations of the system). In a Monte Carlo simulation these different replicas or configurations are generated successively according to a given recipe, and one can then calculate ensemble averages of the properties one is interested in.

4.1   Canonical ensemble

The primitive model simulations are performed at constant (N, V, T) (see also subsection 3.1.3), and under these conditions the replicas of the system which are generated are known as a Canonical ensemble. The (thermal/statistical mechanical) average of an observable Π (e.g., the pressure P) is given by:

$$< \Pi > = \frac{\int \Pi(\mathbf{r}^N) \, exp\left[\frac{-U(\mathbf{r}^N)}{k_B T}\right] d\mathbf{r}^N}{\int exp\left[\frac{-U(\mathbf{r}^N)}{k_B T}\right] d\mathbf{r}^N} \tag{4.1}$$

where the integration is performed over the coordinates of the particles and U is the potential energy for a given configuration of the system. The elements which go into the potential energy function in the primitive model case were given in subsection 3.1.1. The denominator in Equation 4.1 is a particularly important quantity in Statistical Mechanics known as the configurational integral, Z. The relevance is obvious from its relation to the thermodynamic potential of the system:

$$A^{ex} = -k_B T \, ln \, Z \tag{4.2}$$

A^{ex} is the excess part of the free energy, and includes the contributions due to the interactions in the system (i.e., besides the ideal gas term appearing even for $U = 0$). The quantity $(exp\left[-U(\mathbf{r}^N)/(k_B T)\right])/Z$ corresponds to the probability of the system being in a configuration specified by $\mathbf{r}^N$. Of course, in the computer the representation of coordinate space is discrete, not continuous, and the integrals in Equation 4.1 would be replaced by sums over configurations.

It is not feasible to calculate the integrals in Equation 4.1 (and hence Π and even A^{ex}) directly, i.e., by chosing configurations from a uniform (random) distribution over all coordinate space and adding their contributions. The Bolztmann factor $exp\left[-U/(k_B T)\right]$ favours lower energies, and many of the configurations which we would generate with this simple-minded recipe would contribute with essentially zero to the integral (e.g., the energy becomes very high when Lennard-Jones particles start to overlap). The trick in the Monte Carlo method lies in an efficient sampling of coordinate space, concentrating on the regions which have large contributions to the integrals. One generates random configurations of the system with a probability proportional to their Boltzmann factor. In other words, in the end our generated configurations will follow

a Boltzmann distribution, and lower energy states will have been generated more often. When this is done $< \Pi >$ can be simply calculated from a direct average of the values for the M configurations generated with the proper recipe:

$$< \Pi >= \frac{\sum_{i=1}^{M} \Pi_i}{M} \tag{4.3}$$

Let's assume the inital configuration of our slit system is exactly like in Figure 2.1. To create our Boltzmann distributed configurations starting from it one does the following:

- Select a particle at random;

- Displace the particle by a random distance in three dimensional space (this will be a new configuration of the system);

- Calculate the energy difference between the new configuration and the old configuration (the displaced particle sitting where it was before), $\Delta U = U^{new} - U^{old}$;

- Accept the particle displacement (the new configuration) with a probability $min\left(1, exp\left[-\Delta U/(k_B T)\right]\right)$;

- Start from the beginning

The short-hand notation $min\left(1, exp\left[-\Delta U/(k_B T)\right]\right)$ means the following: if $U^{new} < U^{old}$ (i.e., the energy decreases and $exp\left[-\Delta U/(k_B T)\right] > 1$), accept the displacement (the new configuration). Otherwise, generate a random number ξ between 0 and 1. If $exp\left[-\Delta U/(k_B T)\right] > \xi$ the new configuration is accepted. Otherwise, it is rejected and one goes back to (or "keeps") the old one. Enough configurations are generated that the average in Equation 4.3 can be calculated with the desired accuracy. In our slit case, for the different configurations of the system one calculates forces like in Equation 3.9, which are used in Equation 4.3 (and divided by the area) to obtain the final (average) pressures (Equation 3.7). Note that these particle movements or displacements, which generate the different configurations, are what makes our ions "move around" in the system, although the different positions are not linked in time. The Monte Carlo method is purely stochastic.

4.2   Grand-Canonical ensemble

In the molecular solvent studies we now have ions and dipoles in the slit, and both will be subject to the type of displacement moves described in the previous section. A small detail is that for the solvent the particle translations will be coupled to a rotation of the dipole moment vector about one of the molecular axes. The number of ions, the temperature and the volume of the system are constant, but the number of dipoles will fluctuate around an average value. As discussed in subsection 3.2.3, what is kept constant for the solvent is its chemical potential ν_{dip}, and one simulates the equilibrium with a reservoir of bulk fluid. To accomplish this we need two other types of Monte Carlo moves: dipole insertions and dipole deletions. The attempt to insert a solvent particle at a random position in the slit is accepted if

$$\frac{exp\left[\nu_{dip}/(k_BT)\right]V}{(N_{dip}+1)\Lambda^3}\,exp\left[-\Delta U/(k_BT)\right] > \xi \qquad (4.4)$$

where for ΔU one has U^{new} as the potential energy of the configuration with the new dipole, and U^{old} the energy for the configuration without it. These energies now include ion-dipole and dipole-dipole interactions (subsection 3.2.1). The deletion of a randomly chosen dipole is accepted if

$$\frac{N_{dip}\,\Lambda^3}{exp\left[\nu_{dip}/(k_BT)\right]V}\,exp\left[-\Delta U/(k_BT)\right] > \xi \qquad (4.5)$$

Λ is known as the thermal de Broglie wavelength. ξ is again a random number between 0 and 1. The acceptance rule for these moves involves, besides differences in potential energy, the chemical potential of the solvent, which determines how many dipoles one has in the slit, as a function of plate-plate separation. The equation corresponding to 4.1 for the current case is slightly more elaborate[67, 100]. One now has a sum of integrals like the ones in Equation 4.1, since besides the integration over configuration space, *for a given number of dipoles in the system*, one must consider that N_{dip} can in principle assume any value. However, one can be sure that configurations generated from particle displacements accepted with the rule in the previous section and particle insertions/deletions subject to Equations 4.4 and 4.5 will follow the appropriate probability distribution. We can again use a simple average like in Equation 4.3 to calculate $<\Pi>$ at a certain $(\nu_{dip}, N_{ions}, V, T)$.

4.3 Handling long-range electrostatic interactions

We are interested in obtaining mean thermodynamic (macroscopic) properties of a slit system. However, in a computer we can only deal with a certain number of particles. The finite number of particles one decides to handle explicitly, occupying a certain volume, constitutes what is known as a simulation box. One would introduce sizeable (and undesireable) surface effects by just putting walls to confine the system in the directions we actually want it to be infinite (x, y in our slit case). Instead, one uses periodic boundary conditions. Suppose our simulation box is exactly of the size displayed in Figure 2.1 (i.e., a square in the x, y directions with the walls at a certain distance *sep*). When a particle displacement takes the molecule outside of the box in the direction parallel to the plates, it just reenters the simulation volume on the other side. This concept is extensively explained in standard textbooks[67, 100, 101]. One can see that this construction is equivalent to having the simulation box surrounded by replicas of itself. If one attempted move takes the particle to one replica "above" it, another particle will enter the box on the other side, coming from the replica "below" it. There is still one important decision to be taken: how do we treat the interactions which correspond to what is outside our box. After all, there is no guarantee that the properties of the true, infinite system are the same as those for a finite number of particles, even without surface effects. This is not a major issue for intermolecular potentials with a fast distance decay, as is the case of the Lennard-Jones interaction (Equation 3.4). However, it definitely deserves close attention for charge-charge, charge-dipole and dipole-dipole interactions, decaying as r^{-1}, r^{-2} and r^{-3} (Equations 3.1, 3.16 and 3.17, respectively). In these cases the energy contributions from what is outside the box will most likely be sufficiently large to be able to contribute appreciably to the overall behaviour.

Methods to treat long-range electrostatic interactions are a field on their own. See, e.g.,[102] for a recent review. Very popular among them are the so-called Ewald methods[67, 100, 101]. In this case the simulation box is surrounded by infinite replicas of itself. The energy of the system is written as a sum of the interactions in the box plus all the interactions of the particles in the box with their infinite replicas outside. Special mathematical techniques are used to handle these infinite sums. Even though widely used, they are not completely free from criticism. One consequence of the method is that correlations of particles in the box with the outside are enhanced due to the interactions with the infinite

replicas[103]. The underlying physical problem in this thesis work is suffi-
ciently complex that one is well-off without having to struggle with such
technical issues and with finding which method is the "best" for the task.
The approach here has been to take a simple (but reliable!) method of
treating long-range interactions, which in the past had been sucessfully
used in the same kind of systems.

In the so-called charged sheets method[37, 46], the outside of the sim-
ulation box is treated in a mean-field fashion. The ions inside the box
interact with the potential from the average charge distribution outside
the box. This is done self-consistently and for the charge distribution out-
side the box one uses the mean ion distribution sampled in the box during
the course of the simulation. This charge distribution is discretized into
a number of infinite plates or sheets, parallel to the charged walls of
the system, each of them carrying the appropriate surface charge density
σ_i. In each of the infinite charged sheets one must obviously make a
square hole (subtract the potential from a square of smeared-out surface
charge σ_i, see Paper II). This corresponds to the simulation box, where
the interactions are treated explicitly (Equation 3.1). Each ion interacts
with all of these perforated charged sheets. An illustration is given in
Figure 4.1. Note that the interactions in the box are handled with the
so-called minimum-image convention[67, 100], which means that each ion is
always in front of the center of one such square of charge, and in the box
interacts explicitly with the nearest periodic image of all other ions.

The point to stress in this method is that the solution for what is
outside the box is a sensible and understandable physical limit. If we
progressively increase the box size, at some point approximating the
remainder of the system by its mean effect on the simulation volume,
rather than by a sum of individual correlations, should be correct. One
can then simply increase the box size until one gets converged results, and
be confident that after this the external effects can already be adequately
approximated in such a way. It is important to note that the box sizes
needed in this thesis work to get converged results still correspond to
quite manageable systems, i.e., the external mean-field rapidly becomes
a good approximation. Details of the extension of this method to the
molecular solvent cases can be seen in reference[86] and in Paper II. In
this case, besides the charged sheets, one also has sheets representing
the mean polarization profile for the dipoles, which are used to account
for the interactions of ions and dipoles inside the box with the dipoles
outside.

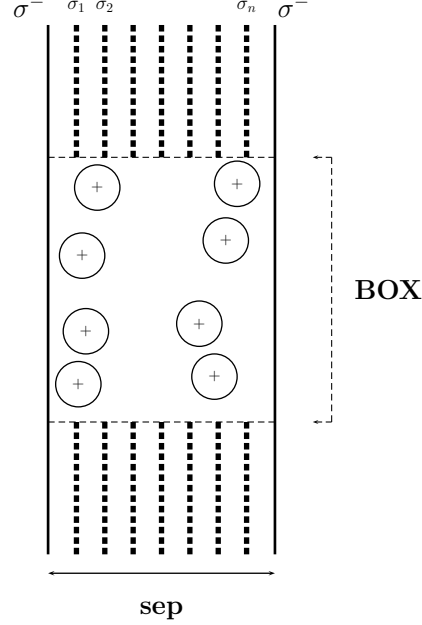The charged sheets method is also interesting in that it affords a di-

Figure 4.1: A schematic illustration of the charged sheets method.

rect "mathematical" interpretation of the ion-ion correlation effect. This is extensively discussed in reference[46] . For the P_{el} term in Equation 3.7 we need to calculate the forces each ion in one half-space feels from the ions and the charged wall on the other half-space. In the context of the charged sheets method this is written as the sum of four terms: ion-infinite charged wall, ion-explicit ions, ion-infinite charged sheets (without the holes) and minus ion-charged squares (to create the holes needed since the forces in the box are considered explicitly through the second term). Due to the properties of the field from an infinite charged surface, Equation 3.8, and to electroneutrality, the first and third terms cancel. The force on one ion is then the sum of the forces from all the ions in the opposite half-space minus the forces from all the charged squares. The latter represent the mean ion distribution, and one then clearly sees that the correlation effect stems from the deviation of the direct ion-ion repulsions from the repulsion afforded by the mean distribution. The former will be smaller than the latter, and one gets an attraction.

4.3.1   The choice of interaction parameters

From Papers II-IV the reader might wonder why I worked with parameters which do not correspond to real ions in real water, so to say. In this case monovalent counterions would have $q = 1e$, divalent $q = 2e$ and for water $\epsilon_r \simeq 80$. One can see from Equation 1.1 that by reducing the charges by 10, and the dielectric constant by 100, the charge-charge interaction at a certain distance will have the same value as in the original system. Something more general can be said looking at the dimensionless parameters which characterize the system in the primitive model[37]. This means that, in a reduced parameter space, the original and the "scaled-down" system are exactly the same. However, in the molecular solvent simulations the interactions are no longer scaled by ϵ_r, and had one worked directly with $q = 1e$ and $q = 2e$ and they would be 80 times stronger than in the PM. Following the approach to introduce difficulties in the studies step-wise, I therefore started with $q = 0.1e$ and $q = 0.2e$ as monovalent and divalent counterions. In this way the treatment of long-range effects is not a major issue when making a comparison between PM and MS force curves sharing a common primitive model description. This obviously also has similar effect on the other long-ranged interactions in the system. Note that in Paper IV the interaction parameters have been increased with respect to the studies in Papers II and III. The take-home message is that this is a measure taken for purely technical convenience, which does not diminish the value of the PM/MS comparisons performed in the studies of this thesis work. The goal is to progressively move towards more "realistic" parameters. Note also that the increase in the interaction parameters might raise other issues, as is suggested in Paper IV. In particular, for sufficiently high q, the modelling of the walls with discrete rather than smeared-out charges can probably have an impact on the force curves in the molecular solvent simulations. This is one clear example where the introduction of more complexity in a controlled fashion contributes to our general understanding of the system and allows one to tackle the difficulties one by one.

Chapter 5

Conclusions

My PhD studies started with a smaller project which once more showed the relevance of the question I was to focus on in the five years which followed. In the Poisson-Boltzmann modelling of the salt screening effect in the DNA-CTA complexes the dielectric description of water worked under quite demanding conditions. The reduction in the DNA-CTA attraction and the increased swelling at progressively higher salt content was quantitatively reproduced in a parameter-free way. Enthalpy data showed an interesting similarity between the dissolution of salt in the complexes, with a limited amount of water, and in the bulk. In the theoretical treatment approximations were made (e.g., the neglect of ion size). However, similar information on how well-behaved the dielectric continuum model can be continues to pile up for a wide range of systems and conditions. It then starts to be difficult to argue that one merely observed a fortuitous error cancellation, and it is perhaps more appropriate to instead ask why.

The systematic studies of double layer forces in Papers II-IV clearly demonstrated that the dielectric screening afforded by a dipolar solvent is reasonably well described by the primitive model with an implicit bulk ϵ_r. This is valid even when it comes to deviations from a mean-field treatment, like the ion-ion correlation attraction. The forces in a molecular solvent have an oscillatory component, as expected even before starting these studies, and which is attributable to packing effects. There is an interplay between ion and solvent packing, and electrostatic interactions influence the oscillations. However, this does not erase the qualitative agreement the dielectric continuum description displays with the MS. In Paper IV the reduction of the solvent size approaching the continuum limit shows decreased oscillations with a period reflecting the solvent size. More importantly, for sufficiently small solvent diameter

one is left with monotonic curves which resemble the PM.

The analysis of free energy curves proves instrumental in these studies. The oscillations are smoothened and the comparison with the primitive model is made easier. The different components of the pressure between the charged walls are also a valuable asset in the interpretation. For the systems of Papers II and III its use was mainly two-fold: identifying common causes for the ion-ion correlation attraction between the PM and the MS; distinguishing effects which are introduced on the MS level, like solvent packing and depletion, from the underlying PM picture.

An important conclusion is that the step-wise approach to the introduction of complexity turned out fruitful and justified. The increase in the electrostatic coupling in Paper IV raised the issue of discrete surface charges, which might have an impact on the MS studies for the given parameters. I note that a hint for the need to introduce discrete surface charges came from recognizing the importance of the electrostatic pressure component for the short-range minimum which appears in the pressure curves. The results obtained in this thesis are from my perspective important and encouraging, but there is still a lot to be done on this problem. This is only a realistic statement and not a declaration of underachievement. Continued thorough and systematic studies are needed, able to separate between model flaws and true physical effects. After mastering the finesses of discrete surface charges it would be interesting to proceed to a more realistic water model. I hope to have contributed to paving the way for these further studies.

Finally, a further nice feature of a slit system is that the determination of the dielectric constant of our molecular solvent can be performed in a quite straightforward (and experimentally related) way by applying an external electric field (Paper V). This is for sure important if one wants to continue making meaningful comparisons between PM and MS results.

I hope that this has constituted a nice appetizer and that you now enjoy the papers!

Popular science summary in english

Charged objects are all around you, even if you do not always stop to think of it. From the shampoo you use, to the food you eat. In some of the most important molecules in your body (lipids, proteins, DNA) and even in the cement which builds your house. They are central to fields so popular nowadays as nanotechnology, drug delivery and biophysics. Water is also everywhere. You obviously wash your hair with it, you have probably seen construction workers mixing cement with water and you should know that it makes up for sixty percent of your body. It should be no surprise that the charges I mentioned exist most of the times in an aqueous environmet. Checklist: charges in water.

(Modern) Physical Chemistry is far more than a "cook and look" (or "mix and look") science. It is devoted to the study of the causes (or mechanisms) for a great deal of important phenomena. Understanding these gives you the power to control the behaviour of many systems, ranging from taylor made materials to the hope for a cure to Alzheimer's disease, where the interactions between charged proteins play a primary role. In the quest for understanding, experiments go hand in hand with theoretical studies and computer simulations, and both are a valuable aid to each other. Updated checklist: understanding; charges in water.

Take cement as an example. When you mix it with water a great deal of microscopic charged particles are formed. You can imagine them as small platelets. For each of these platelets there is a bunch of much smaller mobile charges of opposite sign which make sure the whole thing is electroneutral: its counterions. A platelet with the associated counterions forms what is known as an electric double layer, and the forces between these double layers will dictate if your house will stand or fall down! Cement was only one example, and double layer forces are among the most important properties in many of the systems mentioned before. The level of control and understanding desired cannot do without know-

ing them. New checklist: Double layer; forces; understanding; charges in water.

A system like cement is from a microscopic or molecular point of view very complex, and to do computer simulations we need to use models. These should include the level of detail needed to understand the phenomena we want to study, but cannot be so complex that they become untractable on a computer. Since water is an abundant component in this and many other systems, a common simplification is to describe it as a single number! This number, known as its dielectric constant, scales the charge-charge interactions. This saves a lot of computer hours and allows one to study important and very complex phenomena. Since one sacrificed the molecular detail in this model, known as the dielectric continuum model, it should only work for distances between the charges where water can be seen as a number, rather than a set of molecules. However, there is a lot of evidence that this model is working for very short charge-charge distances, when we would not expect it to.

This thesis deals with simulation studies of charges in dielectric media (of which water is a particularly important example). Coming back to our checklist, the strategy was to perform simulations for the forces between electrical double layers (take the cement platelets as an example) with increasingly more complex models for the solvent. The goal was to understand the peculiar behaviour of the dielectric continuum model at short range. It was found that a more elaborate solvent model, which describes the molecules explicitly, gives double layer forces with which the dielectric continuum model qualitatively agrees. But, as expected, the more elaborate model has features which the simpler continuum model cannot reproduce, mostly connected to molecular size. The agreement between the models happens even for a particularly interesting phenomenon: two platelets of the same charge can attract, rather than repel, which is known as ion-ion correlation attraction. This is certainly not what you learned in school with "likes repel and alikes attract", but it may well be what makes your house stand!

Populärvetenskaplig sammanfattning på svenska

Laddade objekt finns överallt omkring oss, även om du inte alltid tänker på det. Från schampot du använder till maten du äter. I några av de viktigaste molekylerna i kroppen (lipider, proteiner, DNA) och även i cementen som bygger upp ditt hus. De är centrala inom så aktuella ämnen som nanoteknologi, läkemedelsupptag i kroppen och biofysik. Vatten finns också överallt. Du tvättar naturligtvis ditt hår med det, du kanske har sett byggnadsarbetare blanda cement med vatten och du borde veta att din kropp till 60 procent består av vatten. Det borde inte vara någon överraskning att laddningarna jag pratade om oftast förekommer i en vattenmiljö. Checklista: laddningar i vatten.

Modern Fysikalisk Kemi är mycket mer än en "blanda och titta" vetenskap. Dess mål är att studera källorna till (eller mekanismerna bakom) flera viktiga fenomen. Att förstå dem ger en förmåga att kontrollera beteendet hos många system, från skräddarsydda material till möjliga botemedel för Alzheimers sjukdom, där växelverkan mellan laddade proteiner spelar en stor roll. I strävandet efter att uppnå denna förståelse, går experiment hand i hand med teoretiska studier och datorsimuleringar, och de olika metoderna kompletterar varandra. Uppdaterad checklista: förståelse; laddningar i vatten.

Tag cement som ett exempel. När man blandar det med vatten bildas ett stort antal mikroskopiska laddade partiklar. Du kan föreställa dig dem som små flak. För vart och ett av dessa flak finns många mindre, rörliga och oliladdade partiklar (motjoner) som ser till att hela systemet är elektriskt neutralt. En flak tillsammans med sina motjoner utgör ett så kallat elektriskt dubbelskikt, och det kan vara krafterna mellan dessa dubbelskikt som avgör om ditt hus står kvar eller faller ihop! Cement är bara ett exempel, och krafter mellan elektriska dubbelskikt är bland de viktigaste egenskaperna hos många av de system jag pratade om tidigare. Att känna till dessa krafter är nödvändigt för att kunna kontrollera och

förstå dem. Ny checklista: Dubbelskikt; krafter; förståelse; laddningar i vatten.

Ett system som cement är från en mikroskopisk eller molekylär synpunkt mycket komplext, och för att köra datorsimuleringar behöver vi använda modeller. I dessa bör ingå tillräckligt med detaljer för att vi ska kunna förstå de fenomen vi vill studera, men de får inte vara så komplexa att de blir ohanterliga i en dator. Eftersom det finns mycket vatten i detta och i många andra system, är en vanlig förenkling att beskriva vattnet som ett enda tal! Detta tal, den så kallade dielektricitetskonstanten, skalar om växelverkan mellan laddningarna. Denna förenkling sparar många datortimmar och gör det möjligt att studera viktiga och mycket komplexa fenomen. Eftersom man offrar de molekylära detaljerna i denna modell, den så kallade dielektriska kontinuum-modellen, borde den bara fungera för avstånd mellan laddningarna som är så stora att vattnet emellan dem kan beskrivas som en siffra, istället för som ett antal molekyler. Trots detta finns en hel del bevis för att denna modell fungerar för mycket korta avstånd mellan laddningarna, där man inte förväntar sig att den skulle fungera.

Denna avhandling handlar om simuleringsstudier av laddningar i dielektriska medier (av vilka vatten är ett särskilt viktigt exempel). Om vi återvänder till vår checklista, så har strategin varit att köra simuleringarna för krafter mellan elektriska dubbelskikt (exempelvis cementflak) med mer och mer komplexa lösningsmedelsmodeller. Syftet var att förstå den dielektriska kontinuummodellens märkliga beteende vid korta avstånd. Det upptäcktes att en mer detaljerad lösningsmedelsmodell, som beskriver molekyler explicit, ger dubbelskiktskrafter med vilka den dielektriska kontinuummodellen är i kvalitativ överensstämmelse. Men, som förväntat, uppvisar systemet med den mer detaljerade modellen beteenden som den enklare dielektriska kontinuummoddellen inte kan beskriva, vilket huvudsakligen har att göra med molekylernas storlek. Överensstämmelsen mellan modellerna uppstår även för ett särskilt intressant fenomen: att två flak med lika laddning kan attrahera varandra, istället för att repellera. Detta fenomen kallas för jon-jon korrelationsattraktion. Det är säkert inte vad du skulle förvänta dig, men det kan mycket väl vara det som gör att ditt hus står kvar!

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