Electrostatics and stability of self-assembled hollow polyoxometalate shells

Andrei Mlynarchyk

September 11, 2007

Supervisor: dr. René van Roij
Institute for Theoretical Physics
Utrecht University
Abstract

In this thesis we study electrostatics of polyoxometalate (POM) shells which self-assemble from POM macromolecules in low ionic strength solutions. Starting from the well known formulation of the nonlinear Poisson-Boltzmann boundary value problem in a spherical Wigner-Seitz cell for hard-core colloids, we briefly discuss charge renormalization and regulation mechanisms. Subsequently we extend the theory to treat hollow spherical particles, in all respects similar to "ordinary" charged colloids apart from the absence of a hard-core which is replaced with an ionic solution. Applying this extension to a system of POM shells reveals a well-defined shell radius (that minimizes the free energy), although the binding energy is unrealistically large.
Contents

1 Introduction .......................................................... 4
   1.1 Colloids ...................................................... 4
       1.1.1 Ionic solutions ....................................... 5
       1.1.2 Colloidal suspensions ............................... 5
       1.1.3 Inter-colloidal interactions: DLVO theory .......... 6
   1.2 Self-assembled structures. Patchy colloids .................. 7
   1.3 Polyoxometalate (POM) shells ................................ 10

2 Poisson-Boltzmann theory for charged colloids ................. 14
   2.1 Poisson-Boltzmann equation ................................ 14
       2.1.1 Nonlinear Poisson-Boltzmann equation .......... 14
       2.1.2 Linearized Poisson-Boltzmann equation. Debye-Hückel approximation 15
   2.2 Wigner-Seitz cell model .................................. 16
   2.3 Charge renormalization .................................... 17
   2.4 Charge Regulation ......................................... 20
   2.5 Summary ................................................... 26

3 Application of the Poisson-Boltzmann theory to POM shells .... 27
   3.1 Wigner-Seitz cell model for a POM shell ................. 27
   3.2 Numerical studies ......................................... 28
       3.2.1 Electrostatic potential .............................. 28
       3.2.2 Regularized and renormalized charges ............ 32
       3.2.3 Free energy and the equilibrium size of a shell in various solvents ... 36
       3.2.4 Equilibrium size dependence on other parameters of the system .... 42
       3.2.5 DLVO potential. POM shell fluid or crystal? .......... 45
   3.3 Summary .................................................... 47

4 Conclusions and outlook ......................................... 48
1 Introduction

1.1 Colloids

The expression "soft matter" was coined to name a class of substances which can be easily deformed by external forces. Soft matter comprises \textit{e.g.} polymers, liquid crystals, surfactants, colloids.

We will be interested in the latter and their suspensions which play a very important role in everyday life of people. Inks, paints, glues, fog, smog, milk, cream, cheese are just a few examples from a wide variety of substances and phenomena in which colloidal particles\footnote{often referred to as mesoscopic particles, polyions and macroms in the text} are encountered. The presence of colloids in biological liquids like \textit{e.g.} blood has a direct impact on life processes.

For the reasons listed above it is not surprising that properties of colloids, their mixtures with polymers and other components have been thoroughly investigated by scholars from physics, chemistry, biology, medicine departments in many scientific institutions worldwide.

Ranging in size from a few micrometers to several nanometers, carrying surface charges the absolute value of which varies greatly from several tens to many thousands of elementary charges, different in sizes and shapes, colloids are very diverse yet similar in a sense that they are described by the same physical laws and equations. We will further restrict ourselves to spherical particles as they are of primary interest to us.

What is a spherical colloid? The classical approach suggests to view it as a charged hard sphere with a hard-core radius $a$ and a charge $-Ze$, where $e = 1.6 \cdot 10^{-19}$ C the elementary charge. At finite concentrations the system is not ideal and therefore we have to account for inter-particle interactions. The repulsion between two colloids separated by distance $r$ (measured between their centers) will have two following contributions: first, the hard-sphere piece describing hard-core repulsions which reads

$$\phi^{HC}(r) = \begin{cases} 0, & r \geq 2a; \\ \infty, & r < 2a, \end{cases}$$

(1)

where $k = 1.38 \cdot 10^{-23}$ J/K is the Boltzmann’s constant and $T$ the absolute temperature. This means that particles cannot overlap or deform and otherwise do not feel each other unless they get so close that their surfaces touch.

Second, the long-range electrostatic potential of the well known Coulombic form:

$$\phi^{\text{Coul}}(r) = \frac{(-Ze)^2}{\varepsilon r},$$

(2)

where $\varepsilon$ is the dielectric constant of the medium. The expression (2) is not very descriptive if other than two charges are present because the latter affect effective inter-particle interactions and hence can induce additional repulsion or attraction. This is exactly the case if we immerse colloids in ionic solutions. As such systems are of primary interest to us we will elaborate on them and consequently give an improved, more exact expression than (2), describing electrostatics relevant for the above described situation.
1.1.1 Ionic solutions

Consider monovalent salt ions floating around in a molecular solvent. There are two important characteristic lengths of such a mixture. One of them, the Bjerrum length $\lambda_B$, is the distance between two point particles carrying unit charges such that

$$\frac{e^2}{\varepsilon \lambda_B} = kT.$$  

We introduce

$$\beta = \frac{1}{kT},$$

and from the above definition obtain

$$\lambda_B = \frac{e^2}{\varepsilon kT} = \beta e^2.$$  

Another, the Debye length\(^2\) $\lambda_D$, is defined as follows:

$$\lambda_D = \left(\frac{8\pi e^2 \rho_s}{\varepsilon kT}\right)^{-1/2},$$

where $\rho_s$ denotes equal densities of positive and negative salt ions. The Debye and the Bjerrum lengths are obviously related:

$$\lambda_D = (8\pi \lambda_B \rho_s)^{-1/2}.$$  

A very popular approach to study ionic solutions is called the primitive model. Within its framework, first of all, the solvent is treated as a continuous incompressible medium with a uniform dielectric constant $\varepsilon$. Second, microions are assumed to be hard spheres with point charges $\pm q$ in their centers. Third, the charge neutrality condition holds true which means the numbers of positive $N_+$ and negative $N_-$ ions are equal:

$$N_+ = N_- = N.$$  

If in addition the radii of plus- and minus-ions are equal then such system is called the restrictive primitive model.

1.1.2 Colloidal suspensions

Now that we have described the ionic solution we add a colloid to it. Normally neutral in the air, in polar solvents it acquires a non-zero surface charge, say $-Ze$, due to electrolytic dissociation. The equal charge of opposite sign is of course simultaneously stripped off the surface and injected into the reservoir. Observe that the total charge neutrality condition is not violated:

$$-Ze + Ze + N_+q + N_-(-q) = 0.$$  

We immerse more and more colloids and get a colloidal suspension. Like-charge macroions tend to repel each other via long-range Coulombic forces and prevent colloids from aggregation - a suspension is charge-stabilized. At high enough $Z$ and large enough $\lambda_D$ the

\(^2\)called also Debye screening length for the reasons that we will discuss later on in this script
electrostatic repulsion is so strong that weak attractive van der Waals forces cannot compete it and hence phase separation does not occur. This property of colloidal suspensions is of great importance for industry, technology and biological processes.

Experimental accessibility of length-scales make solutions and dispersions of polyions attractive for modeling real molecular and atomic systems. The parameters of this model are easily tunable: one can vary ionic strength, types of solvents, their pH to influence phase behavior. Such studies have revealed that under certain conditions Brownian colloids can make a transition to crystalline order. Crystals which are formed do not often resemble those encountered in solid state physics: these structures may be very dilute with lattice constants many times bigger than colloidal diameter [1]. A wide variety of such unusual lattices are enjoying special attention nowadays being a field of detailed studies [2].

Theoretical research and computer simulations have long been very important tools to describe colloidal suspensions and explain their phase behavior in various regimes. The complications these studies have to overcome originate from large size and charge asymmetry (between mesoscopic particles on one side and microions on the other) which prohibits treating all components on equal footing.

Even if one succeeds tracing colloidal coordinates explicitly, the primitive model of an ionic solution is still very complicated due to the fact that each microion has to be accounted for. An efficient way of avoiding this is the replacement of individual ions by their mean density profiles $\rho_\pm(r)$. After averaging out microionic degrees of freedom we obtain an effectively one-component system of colloids.

It is worth noticing that there are studies which describe microions explicitly and even attempts to go beyond the primitive model and include the effects of solvent granularity [3], or multicomponent nature of various solvents [4]. This is of course admirable but certainly makes matters more complicated.

1.1.3 Inter-colloidal interactions: DLVO theory

We established that colloidal suspensions are interacting systems. This is due to the fact that they can roughly be considered as mixtures of charged spheres (plates, rods etc.) floating around in some solvent in the presence of microions. Electrostatic forces therefore have a direct impact on behavior of such systems.

We came to the conclusion that Coulombic dependence (2) cannot be employed for the case at hand as it does not reflect all involved physics. The important question then is how to describe inter-particle interactions in a suspension.

We consider two identical spheres of radius $a$ placed in some continuous isotropic solvent with suspended salt such that the Debye length is $\lambda_D$. We further assume their (equal) charges are smeared homogeneously over the surfaces. In this case spherical symmetry is gained and to know the electric potential in each space-point around the colloid it is sufficient to calculate it once along any radial line. Equipotential surfaces in this simple yet accurate formulation are just concentric spheres.

Derjaguin with Landau and independently Verwey with Overbeek [5] demonstrated that the repulsive electrostatic potential for such system is of the Yukawa form:

$$V_{DLVO}(r) = \frac{Z^2 e^2}{\varepsilon} \left( \frac{e^{\kappa a}}{1 + \kappa a} \right)^2 e^{-\kappa r} \frac{e^{-\kappa r}}{r},$$

(7)
with \( \kappa = 1/\lambda_D \).

This is a traditional starting point for studying the behavior of charged colloids, provided that short-ranged van der Waals attractions and quantum effects in the close vicinity of their surfaces can be ignored (which is normally the case). Observe that the potential depends on the properties of all "parties" - solvent, salt and macroions. This is why it is of great importance that we make valid and legitimate assumptions about them.

The fact that the potential is not of the familiar Coulombic form, i.e. \( \sim 1/r \), but rather \( \sim e^{-\kappa r} \) is due to the electrostatic screening effect. Consider, say, negatively charged colloidal surface. Then positive counterions will tend to get closer to the macroparticle enveloping it with a dense cloud whereas negative coions will be repelled further away by a huge colloidal charge. The positively charged cloud of counterions is called an electric double layer and in a sense screens the polyclion making the electrostatic potential fall off more rapidly, on a typical distance given by the Debye screening length (6).

In some cases it may be useful to distinguish between the innermost part of the microionic cloud, the so called Stern layer consisting of counterions adsorbed, glued to the macrion’s surface by strong attractive forces, and the diffuse part that fills up the remaining volume of the electric double layer.

The celebrated expression (7) has however its shortcomings. This manifestly repulsive potential does not predict cluster formation and phase separation in some cases reported recently. For example, it was shown that the effective force between two spherical colloids in an ionic solution may turn attractive if correlations between microins are properly accounted for [6].

Since the behavior of any system is governed by its free energy \( F \), we expect that pairwise DLVO repulsions give rise to just one of the contributions to it. This means that attractive term(s) must be added to (7) in case phenomena like liquid condensation, chain (plane, sphere etc.) formation or aggregation in more complex structures are reported.

Admittedly, at low salinity short-range van der Waals attractions cannot lead to phase separation because the colloids cannot jump into this minimum over high repulsive DLVO barrier. This implies that long-range attractive forces do exist. There are many suggestions and attempts to explain the origin of those forces. As this is on its own a longstanding concern and a vast topic of research we will just name the following without going into detail: hydrodynamic coupling [7], image charges [8], three-body effects [9], divalent salt ions [10]. All these can induce inter-colloidal attractions and lead to separation in a denser phase - liquid and a more dilute - gas.

### 1.2 Self-assembled structures. Patchy colloids

Some soft matter systems are known to have a potential to self-organize themselves into regular complex structures. This is a spontaneous process, governed by thermodynamics without any direct mechanical contact with the particles, called self-assembly.

Thermodynamic equilibrium brings any system into the state for which the free energy \( F \) is minimized. If aggregation into chains, sheets, spherical or cylindrical etc. structures favors lowering \( F \) then monomers will prefer to self-assemble in such clusters. Examples of those include a wide variety of shapes encountered in biology (like virus capsids, micelles, bilayers, membranes, vesicles) and crystalline structures familiar from solid state physics.
Traditional 3D bulk agglomeration is possible if we assume that interactions between colloidal particles are isotropic, i.e., each element on one particle’s surface can form a bond with any spot on another’s. Irregular polydisperse clusters of quite random geometry will be formed then. This type of agglomeration, being typical, is however not the only possible one.

Intuitively clear, aggregation in ordered, regular clusters of non-random shape is a somewhat different phenomenon. Why do preferred directions of growth exist? What can break space symmetry? The answer is that anisotropy in this case is inherent and predefined by properties of the colloidal surface. It turns out that some macroparticles have so called “sticky patches” which are attracted to similar sites on other particles. Places on the surface other than the sticky ones are non-bonding and therefore irrelevant for the process of cluster formation. In fig.1(a) we present a patchy particle with an “attractive equatorial circle”. Single layer planar sheets can be formed from this type of monomers(fig.1(b)).

Sticky sites on the surface of a patchy particle are discrete and limited in number. They can be selective, i.e., tend to pair up with some and ignore or repel other types of patches. Some more examples of particles with sticky sites can be viewed in fig.2. The monomers depicted in fig.2(a) obviously can aggregate in chains only, whereas (b-e) can form quite complex yet geometrically regular structures.

A remarkable aspect of particles which interact along preferential directions is their rich cluster formation. Shape and size of these clusters depend on (i) the geometry of monomers and the surface distribution of sticky sites, (ii) the parameters of the system which influence

\footnote{for example, in DNA molecules an amino acid monomer glues to exclusively the complementary one}
Figure 2: Patchy particles. (a) Side and front view of a spherical patchy particle with two diametrically opposed circular patches. (b,c) Front views of two patchy spheres with differently patterned ring-shaped patches. (d,e) Two patchy spheres with double-ring patches shifted off the equatorial plane.
the strength of attractive interactions between monomers (temperature, salt concentration, pH etc.).

If one knows how the sticky patches are distributed and how interactions depend on driving parameters then one gains control over behavior of monomers in a solution. Rather than manipulating tiny particles mechanically one will have to place them into an environment with certain physical and chemical characteristics which favor self-assembly. An exciting potential application of having this control is synthesis of nanosized structures with predictable geometrical, chemical, electronic, optical properties.

Self-organization of matter is, in my opinion, a very beautiful and thrilling phenomenon which can be extended far beyond a reservoir with a colloidal suspension.

1.3 Polyoxometalate (POM) shells

In this section we introduce a very exciting and beautiful product of nanochemistry - polyoxometalate shells. A group of researchers from Utrecht University have recently successfully conducted experiments in which they witnessed the formation of spherical single-layer hollow superstructures - POM shells - self-assembled from POM monomers immersed in solvent under condition of low ionic strength. The shells were proven to have a clear monolayer surface and a nearly monodisperse radius. This is quite surprising as each shell consisted of more than 1000 individual building blocks (abbreviated as $\text{Mo}_{72}\text{Fe}_{30}$ and $\text{Mo}_{132}$), in their turn being some of the largest inorganic macromolecules.

Polyoxometalates comprise a wide variety of transition metal-oxygen nanosize clusters. Shapes of the latter are geometrically regular. In addition to large size and structural symmetry POMs possess remarkable electronic properties which make them suitable building blocks for construction of inorganic-organic hybrid materials. A wide variety of possible exciting applications of these compounds have been anticipated in catalysis [11], materials science [12], medicinal chemistry and biochemical analysis [13]. Bleaching of paper and corrosion protection are among important industrial tasks where POMs could be useful. The property of POMs to exhibit different colors in different states and their photochemical stability suggest that dyes based on them might be a way better than organic counterparts.

It is not surprising therefore that POMs have been objects of tremendous interest for already several decades. New areas of research and possible applications arose after published evidences that some of these giant spherical and wheel-shaped molecules have a potential to slowly self-assemble into more complex highly ordered superstructures like vesicles [14], multilayers [15] and shells [16] which we address in this thesis. We will be interested in hollow spherical shells consisting of molybdenum containing POM macromolecules. Previously it was already shown that individual copper- or tungsten-based POMs can also self-organize to form similar structures [17].

$\text{Mo}_{72}\text{Fe}_{30}$ and $\text{Mo}_{132}$ (see fig.3(a)) are representatives of the big family of POMs. They are spherical metal oxide clusters of diameters 2.5 and 2.9 nm, respectively. When placed in a polar solvent, these molecules acquire a surface charge. Under low ionic strength condition POM monomers start to slowly (taking a few weeks - months [18]) self-assemble in a spherical superstructure. Formation of the shell can be accelerated by heating up the

---

4 Self-organization processes are encountered in physics, chemistry, biology, cybernetics, economics, human society etc.
Figure 3: Polyoxometalate macromolecules $Mo_{132}$ and $Mo_{72}Fe_{30}$ (a) and a sketch of a POM shell (b). Top picture (a): POMs - highly symmetric nanosize inorganic molecules. Bottom (b): the monomers depicted above can self-assemble in a single layer spherical shell.
Figure 4: POM shell radius as a function of the inverse relative dielectric constant of the solvent for two polyoxometalates: $Mo_{72}Fe_{30}$ and $Mo_{112}$. The slope of the line is given by $3824 \pm 266$ nm.

bath to $T \simeq 323$ K which helps monomers to acquire kinetic energy sufficient to overcome the DLVO barrier, get close and stick to each other. Instead of forming a planar sheet which requires zero bending energy POMs for yet unknown reasons prefer to fold in a single layer, hollow spherical droplet. The surface of this sphere is covered by closely packed POMs which probably bind to each other via hydrogen bonds (see fig.3(b)).

As discussed, this type of clusters can be formed if building blocks belong to a class of patchy particles with directional attractive inter-monomer forces. The exact origin of these attraction has not yet been clarified and a convincing explanation why POM shells are stable has been actively sought for.

There is a strong evidence coming from electron microscopy that shells have very regular surfaces which are nearly monodisperse-sized spheres without observable defects. Radii of the superstructures lie in the range between 20 – 100 nm and are proportional, as experiment shows (see fig.4), to the inverse dielectric constant of the solvent in which shells drift around.

To summarize, we have a system of identical charged spherical shells suspended in an homogeneous molecular solvent in the presence of very low concentration of salt. By all means the setup looks like that of an ordinary colloidal suspension. The only difference is that this "colloid" is a bit exotic - it has no hard-core interior but is filled with solvent and microions instead.
To treat this non-trivial system quantitatively we need to introduce the theory which describes the behavior of suspensions of charged hard-core colloids first, and then to extend it to the case of complex spherical super-particles with voids and an additional inner electric double layer, using POM shell as an example of the latter.

We believe these studies are not only useful for elucidating why polyoxomolybdate shells are stable but they might be relevant for description of a wide variety of recently synthesized hollow particles suspended in ionic solutions.
2 Poisson-Boltzmann theory for charged colloids

2.1 Poisson-Boltzmann equation

2.1.1 Nonlinear Poisson-Boltzmann equation

We agreed upon the way of treating colloidal suspensions in the previous chapter of the thesis. After averaging out microionic degrees of freedom we obtained an effectively one-component system of mesoscopic particles. In this mean-field approximation the Hamiltonian of the system of \(N\) identical colloids reads

\[
\beta H (\{R_i\}) = \sum_{\alpha = \pm} \int dr \rho_\alpha (r) \left[ \ln \frac{\rho_\alpha (r)}{\rho_s} - 1 \right] + \frac{1}{2} \int dr \left[ \rho_+ (r) - \rho_- (r) + q(r) \right] \phi(r) + \sum_{\alpha = \pm} \int dr \rho_\alpha (r) \beta \phi_H^{HC} (r),
\]

where \(\{R_i\}\) denotes the set of coordinates of colloidal centers, \(i = 1..N\), \(2\rho_s\) is the total ion density in the absence of polyions, \(\rho_\pm (r)\) are the ionic density profiles introduced in the previous section and \(\phi(r)\) the dimensionless electrostatic potential. The first term of the Hamiltonian comprises the microionic entropic contributions, the second accounts for electrostatics (with \(q(r)\) the colloidal charge distribution), and \(\phi_H^{HC}(r)\) is a familiar hard-core potential introduced in (1).

We now proceed to calculate the equilibrium density profiles which minimize the functional (8). Assuming that charges cover the colloidal spheres homogeneously, we write down their distribution

\[
q(r) = \sum_{i=1}^{N} \frac{-Z}{4\pi a^2} \delta(|r - R_i| - a),
\]

and subsequently define the dimensionless electrostatic potential in integral form as

\[
\phi(r) = \lambda_B \int dr' \frac{\rho_+ (r') - \rho_- (r') + q(r')}{|r - r'|}.
\]

The latter becomes in differential form

\[
\nabla^2 \phi(r) = \lambda_B \int dr' \left[ \rho_+ (r') - \rho_- (r') + q(r') \right] \nabla^2 \frac{1}{|r - r'|^{-1}} = -4\pi \lambda_B \int dr' \left[ \rho_+ (r') - \rho_- (r') + q(r') \right] \delta(r - r')
\]

\[
= -4\pi \lambda_B \left[ \rho_+ (r) - \rho_- (r) + q(r) \right],
\]

in which we recognize Poisson’s equation.
From the minimum of the Hamiltonian (8)
\[
\frac{\delta \beta H}{\delta \rho_\pm (r)} = 0 = \ln \frac{\rho_\pm (r)}{\rho_s} \pm \phi (r) + \beta \phi_H^C (r)
\]  
we recover the equilibrium density profiles in the subspace outside the colloidal cores - the familiar Boltzmann law:
\[
\begin{align*}
\rho_+ (r) &= \rho_s \exp[-\phi (r)]; \\
\rho_- (r) &= \rho_s \exp[+\phi (r)].
\end{align*}
\]  
We introduce the Debye screening parameter
\[
\kappa = (8 \pi \lambda_B \rho_s)^{1/2},
\]
(note the relation \( \kappa = \lambda_D^{-1} \)) and using the minimum condition (12) and the Poisson equation (11) we derive the nonlinear Poisson-Boltzmann equation with the corresponding boundary conditions
\[
\nabla^2 \phi (r) = \kappa^2 \sinh \phi (r);
\]
\[
\hat{n}_i \cdot \vec{\nabla} \phi (R_i + a \hat{n}_i) = Z \lambda_B / a^2,
\]
where the first relation refers to the the region outside the colloidal cores and the second to the colloidal surfaces, \( i = 1..N \). If one wants to solve electrostatic problem rigorously, one has to consider (15), i.e. a nonlinear partial differential equation with multicentered boundary conditions.

2.1.2 Linearized Poisson-Boltzmann equation. Debye-Hückel approximation

The nonlinear Poisson-Boltzmann equation (15), unfortunately, cannot be solved analytically. To overcome this unpleasant complication Debye and Hückel in 1923 [19] proposed a linearization scheme the essence of which is to make a replacement \( \sinh \phi \approx \phi \) if the electric potential in the system of interest is sufficiently small. Consequently (15) can be rewritten as
\[
\nabla^2 \phi (r) = \kappa^2 \phi (r);
\]
\[
\hat{n}_i \cdot \vec{\nabla} \phi (R_i + a \hat{n}_i) = Z \lambda_B / a^2,
\]
where the screening parameter is, as before,
\[
\kappa = \lambda_D^{-1} = (8 \pi \lambda_B \rho_s)^{1/2}.
\]
Equation (16) can be solved analytically in simple geometries. So if microions are monovalent and the electrostatic potential \( \phi \) at the colloidal surface is \( \approx 0.25 \) mV or smaller at room temperature [20] then one may linearize the problem (15). If on the other hand surface potentials are large, like it can be for latex particles or ionic micelles, the Debye-Hückel approach is inaccurate and one should be aware of drastic discrepancies with reality. For example, the solution of the linearized equation (16) may predict a thermodynamic instability.
and an associated phase separation into coexisting gas and liquid phases whereas numerical studies of the equation (15) give no indication to it [21].

In what follows we refrain from employing the Debye-Hückel approximation and prefer to retain nonlinearity of the problem (15) as we believe taking it into consideration might be crucial for the description of a POM shell formation.

Even though we made already several approximations in the previous chapters, the many-body character of the Poisson-Boltzmann equation (15) still makes matters complicated. Without severe distortion of the relevant physics several techniques have been developed which help to resolve the computational problems. The most popular of those - the cell model - will be discussed in the next paragraph.

2.2 Wigner-Seitz cell model

In this section we give a brief overview of the Poisson-Boltzmann (Wigner-Seitz) cell model - a popular approach to study suspensions of colloidal particles. The idea is that each polyion together with a part of surrounding microionic cloud is confined to an imaginary cell of the corresponding geometry. For example, rod-like particles are surrounded by cylindrical cells, spheres - by spherical, etc.

By construction such an approach has the virtue of preserving the nonlinear character of the Poisson-Boltzmann equation (15). Computationally great simplification is regained because all cells are postulated to be identical. Hence we have to find the solution of (15) in one cell only rather than calculate potentials around each macroion.

The essence of division into cells is quite straightforward: consider a system of volume $V$ and assume the number of identical colloidal particles of radius $a$ suspended in it $N$ is constant. The cell volume then is just $V/N$ and its corresponding radius $R = a/\eta^{1/3}$, where

$$\eta = N \cdot \frac{4\pi a^3}{V}$$

stands for the packing fraction of colloids. Some studies suggest including a close packing factor for spherical particles $\eta_{\text{max}} \approx 0.74$, so that $R = a(\eta_{\text{max}}/\eta)^{1/3}$, but we prefer to employ the first approach.

The next assumption is that Wigner-Seitz cells are charge neutral, in other words, the sum of the surface charge and all co- and counterions within the cell is precisely 0. Charge neutrality implies that the electric field $E$ at the cell boundary vanishes. Because the field strength is the minus gradient of the potential,

$$E(r) = -\nabla \phi(r),$$

the latter must be flat at the cell boundary:

$$\frac{d\phi(r)}{dr} \bigg|_{r=R} \equiv 0.$$  \hspace{1cm} (18)

Given the symmetry of the problem (15) in the cell formulation, it is natural to go to spherical coordinates where we have to replace the Cartesian Laplacian with the following expression:
\[ \nabla^2_{\text{spher}} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \frac{\partial}{\partial r} \phi(r) \right]. \]  

(19)

We omit the angular part of the operator assuming spatial isotropy and symmetry of charge distribution within the cell. Using in addition the extra boundary condition (18) we can now reformulate the full nonlinear Poisson-Boltzmann equation (15) within the framework of the cell model:

\[ \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \frac{\partial}{\partial r} \phi(r) \right] = \kappa^2 \sinh \phi(r); \]  

(20)

\[ \phi'(a) = \frac{Z \lambda B}{a^2}; \]

\[ \phi'(R) = 0. \]

The Wigner-Seitz cell approach to study colloidal suspensions was employed by Alexander \textit{et al.} in their famous research on charge renormalization (we elaborate on this in the next section) in spherical geometry [22]. It has as successfully been applied for colloids of cylindrical and parallelepipedic shapes [23]. Despite alternative models like \textit{e.g.} renormalized jellium [24] are being developed nowadays, the validity of the cell prescription has not been shaken.

From (20) one can immediately appreciate the reduction of the computational effort: we still need to solve a second order nonlinear differential equation but now in one cell only and moreover a one- rather than three-dimensional radial grid is quite a simplification. Shooting from the boundary of the cell with some definite value of the potential \( \phi(R) \equiv \phi_R \) and the zero slope we calculate \( \phi \) in the next grid point using a finite difference scheme and iteratively arrive at the colloidal surface with the desired derivative \( Z \lambda B/a^2 \).

A typical solution of the boundary value problem in the last formulation (20) and the corresponding microionic distributions calculated according to the Boltzmann law

\[ \rho_\pm(r) = \rho_s \exp \left[ \mp \phi(r) \right] \]

are plotted in fig.5(a),(b). As expected, the density profile of the counterions hits its maximum in the close vicinity of the colloidal surface and gradually falls off to the cell boundary. The concentration of like-charge coions on the other hand increases towards it.

We have briefly described the Wigner-Seitz cell model. It is appropriate not only or specifically for spherical macroions but can be equally efficiently applied in other geometries. Generically the most convenient shape of the cell is that of the particle confined to it together with its electric double layer of typical thickness \( \lambda_D \) (6).

2.3 Charge renormalization

The observation that a macroparticle together with a part of its surrounding microions may be considered as an entity underlies the principle of charge renormalization developed by Alexander [22].

While like-charge ions are repelled towards the cell boundary, counterions experience strong electrostatic coupling to the surface. Some of them make the dominant contribution
Figure 5: Top graph (a): the electrostatic potential for the case of the bare colloidal charge \( Z = 1000, \kappa a = 3.0, a = 133 \text{ nm}, \lambda_B = 0.72 \text{ nm} \) and the packing fraction \( \eta = 1/8 \) corresponding to the radius of the Wigner-Seitz cell \( R = 2a \). Bottom (b): the microionic densities and the charge density \( \rho(r) = \rho_+(r) - \rho_-(r) \) (normalized to \( \rho_s \)) corresponding to the potential depicted in the top figure.
Figure 6: The electrostatic potential $\phi(r)$ for a system with $\kappa a = 3.0$, $a = 72$ nm, $\lambda_B = 0.72$ nm, $R/a = 1.5$ and $Z = 10^4$. The effective charge $Z^* \approx 2200$ is determined by the derivative of the potential at the colloidal surface $\phi'(a)$.

to the ionic cloud which embraces the mesoscopic particle, some condense onto the colloidal sphere forming a thin counterionic "coat" - the Stern layer. As a result the absolute value of the net charge of such dressed colloid\(^7\), $Z^*$, is smaller than that of the bare one\(^8\) $Z$. Hence charge renormalization has a natural explanation from a physical point of view.

Mathematically the procedure of renormalization is essentially a replacement of the nonlinear solution $\phi(r)$ with a simplified Debye-Hückel approximation $\phi_{lin}(r)$ matching the latter with the former at the cell boundary:

$$\phi_{lin}(r) = \phi_R + \tanh \phi_R \left( \nu_+ \frac{\lambda_B}{r} e^{\kappa(r-R)} + \nu_- \frac{\lambda_B}{r} e^{-\kappa(r-R)} - 1 \right),$$

(21)

with $\phi_R$ the solution of the nonlinear problem (20) at the cell boundary,

$$\kappa = \kappa \sqrt{\cosh \phi_B},$$

(22)

and

$$\nu_\pm = \frac{\kappa R \pm 1}{2\kappa \lambda_B}.$$ 

(23)

The purpose of doing this is to preserve the DLVO form of the interaction (7) (derived within a linear theory) for the case of highly charged colloids (for which linearization is inapplicable

\(^7\)called renormalized, or effective charge and denoted by $Z^*$ or $Z_{eff}$

\(^8\)called bare, or structural charge and denoted by $Z$ or $Z_{bare}$
due to high potentials). One can still use the expression (7) with the only difference that the bare charge $Z$ has to be replaced by the corresponding effective one $Z^*$.

It was shown in [25] that to calculate $Z^*$ it is sufficient to know the solution of the nonlinear boundary value problem (20) at the cell boundary $\phi_R$:

$$Z^* = \frac{\tanh \phi_R}{\bar{\kappa} \lambda_B} \{(\bar{\kappa}^2 a R - 1) \sinh[\bar{\kappa}(R - a)] + \bar{\kappa}(R - a) \cosh[\bar{\kappa}(R - a)]\}. \quad (24)$$

The effective charge (24) governs intercellular electrostatic repulsions and determines the microionic distributions within an individual cell sufficiently far away from the colloidal surface, where the potential is reasonably flat and the Debye-Hückel solution (21) is close to the nonlinear - the "true" one (fig.6).

In fig.7 we plot several curves illustrating the dependence of the effective charge on the structural one for several values of the (dimensionless\(^9\)) product $\kappa a$. It turns out that $Z^*$ can nearly be coinciding with $Z$ for low colloidal bare charges (see fig.7(a)), while it can be orders of magnitude smaller than $Z$ for high $Z$ (fig.7(b)). This points to the fact that linearization is a valid scheme to calculate electrostatic potentials and microionic density profiles within Wigner-Seitz cells if the suspension is in the low colloidal charge regime. Otherwise nonlinearity of the Poisson-Boltzmann equation close to the surfaces of polyions has to be retained.

We further consider the dependence of the effective charge on the salt concentration keeping other parameters of the system fixed, and varying only $\rho_s$, or equivalently $\kappa a = (8\pi \lambda_B \rho_s)^{1/2} a$. From the graph presented in fig.8(a) we readily conclude that no significant renormalization occurs in the high ionic strength regime. Similarly, as we make the colloidal suspension denser the effective charge approaches the bare one. From fig.8(b) we read off that in the limit of close packing the effect of renormalization becomes negligible whereas for dilute systems it must definitely be taken into account.

In this section we have given a brief introduction to charge renormalization - the mechanism caused by strong Coulombic attraction of counterions to the oppositely charged surface of a mesoscopic particle. This microionic cloud screens the polyion. As a result the colloidal charge appears to be smaller than it is in fact, and therefore effective repulsions between cells containing counterion-colloid entities are reduced.

### 2.4 Charge Regulation

In the previous sections we formulated the boundary value problem within the framework of the Wigner-Seitz cell. Given the bare charge on the colloidal surface we solved the system of equations (20) and immediately calculated the effective charge in terms of the potential at the cell boundary $\phi_R$ using (24).

There is however one subtle but very important detail we have not yet touched upon. It is not typically the case that mesoscopic particles carry definite fixed surface charge. In fact the bare charge $Z$ is a dynamic variable which depends on physical and chemical properties of the colloid, the solvent and the added salt and has to be calculated when equilibrium between ionized surface groups (like sulphate, carboxylic etc.) and free ions is reached.

\(^9\)It is preferable to use dimensionless quantities in numerical studies, and we respect this convention where possible
Figure 7: The effective charge as a function of the structural charge. Here $a = 133$ nm, packing fraction $\eta = 1/8$ which corresponds to $R = 2a$, $\lambda_B = 0.72$ nm are kept fixed. Top graph (a): the values of the effective charges nearly coincide with those of the structural in the low-charge region. Bottom (b): the effective charges for various $\kappa a$ approach some definite values called the saturated charges and do not increase any further beyond them.
Figure 8: Charge renormalization as a function of the screening constant (a) and the packing fraction (b), in both cases for $Z = 1000$, $a = 133$ nm, $\lambda_B = 0.72$ nm. Renormalization may be very important at low salt concentrations and in dilute suspensions.
We consider a colloidal sphere of radius $a$ and $M$ ionisable sites on its surface. The maximum number of charged groups is therefore $M$, but only $Z$ of them are actually charged, where $Z$ is to be determined as follows. We write down the cell model grand potential for the system of colloidal particles in an ionic solution:

$$
\beta \Omega[\rho_{\pm}(r), Z] = \sum_{\pm} \int \! \!dr \rho_{\pm}(r) \left[ \ln \frac{\rho_{\pm}(r)}{\rho_s} - 1 \right] + \frac{1}{2} \int \! \!dr [\rho_+(r) - \rho_-(r) + q(r)] \phi(r) + \beta F_s(M, Z). \tag{25}
$$

Here we assume the integrals to be performed over a Wigner-Seitz cell interior. The first and the second lines of this expression are identical to those encountered in (8). The last one describes the non-electrostatic piece of the surface free energy of the polyions:

$$
\beta F_s(M, Z) = -\ln \left( \frac{M}{Z} \right) + Z \beta E, \tag{26}
$$

with $E$ - the binding free energy\textsuperscript{10} of each site on the surface of the macroparticle. The expression (26) comprises the entropy of $Z$ ionized sites out of $M$ available, and the binding energy of all surface groups that dissociated. Recalling the equality

$$
\binom{M}{Z} = \frac{M!}{Z!(M-Z)!}, \tag{27}
$$

and using the Stirling formula, we can rewrite

$$
-\ln \left( \frac{M}{Z} \right) \simeq Z \ln \frac{Z}{M-Z} - M \ln \frac{M}{M-Z}. \tag{28}
$$

We substitute (28) into the grand potential (25) and minimize the latter w.r.t. $Z$ which yields

$$
\ln \frac{Z}{M-Z} = \phi(a) - \beta E,
$$

from which the equilibrium (regulated) charge follows:

$$
Z = \frac{M}{1 + \exp[\beta E] \exp[-\phi(a)]}. \tag{29}
$$

This expression makes a bridge between the bare charge of the colloidal particle and the maximum number of dissociable sites $M$ on its surface, their ionization energy $E$ and the solution of the Poisson-Boltzmann equation (20) at the surface of the colloid. It is more convenient to re-express the regulated charge in terms of the dissociation constant $K$ which is normally known in experimental setups and can be related to the ionization energy:

$$
K = \rho_s \exp[-\beta E]. \tag{30}
$$

\textsuperscript{10}equivalently, ionization free energy
The structural charge of the colloidal particle can now be written in terms of $K$:

$$Z = \frac{M}{1 + \frac{\rho_s K}{\epsilon} \exp[-\phi(a)]}. \quad (31)$$

We assumed that ionizable groups are homogeneously distributed over macroion’s surface with the uniform charge density

$$q(r) = -\frac{Z}{4\pi a^2} \delta(r - a), \quad (32)$$

and now substitute (28), (32) in the grand potential of a spherical Wigner-Seitz cell (25):

$$\beta \Omega = 4\pi \rho_s \int_0^R dr r^2 \left\{ \phi(r) \sinh \phi(r) - 2 \cosh \phi(r) \right\} - \frac{Z}{2} \phi(a)$$

$$- Z \ln \frac{Z}{M - Z} + M \ln \frac{M}{M - Z} + Z\beta E. \quad (33)$$

The latter with (30) becomes

$$\beta \Omega = 4\pi \rho_s \int_0^R dr r^2 \left\{ \phi(r) \sinh \phi(r) - 2 \cosh \phi(r) \right\} + \frac{Z}{2} \phi(a) - M \ln[1 + \frac{K \rho_s}{\epsilon} \exp[\phi(a)]] \quad (33)$$

Note that $Z$ in (33) has to be calculated according to (31), and that $\phi(r)$ is a solution of the boundary value problem (20) with charge regulation included:

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \frac{\partial}{\partial r} \phi(r) \right] = \kappa^2 \sinh \phi(r); \quad (34)$$

$$\phi'(a) = \frac{\lambda B M}{a^2 \left[ 1 + \frac{K}{\epsilon} \exp[-\phi(a)] \right]};$$

$$\phi'(R) = 0.$$

To give a better feeling of regulation and to characterize its impact quantitatively let us consider the following example which will be used later on to describe POM shells. Assume that all the ionisable sites are identical and have circular cross-sections of diameter $d$. They are packed closely to each other on the surface of a spherical colloid and carry $M_1 = 30$ ionisable groups each. The maximal possible charge $M$ of the colloid of radius $a$ is then obviously

$$M = \frac{16a^2}{d^2} M_1. \quad (35)$$

For such a colloid we graphically demonstrate the dependence of its bare and renormalized charges on $M$ in fig.9. One can expect that the bare charge will continuously and steadily grow if the radius of the colloid increases further, whereas the bottom curve will become parallel to $M$-axis when the saturated value of the effective charge will be hit.
Figure 9: Bare colloidal charge $Z_{\text{bare}}$ and its renormalized value $Z^*$ as a function of $M$. Note that as the number of ionizable sites increases both structural and effective charges also increase. Observe and appreciate that $Z_{\text{bare}}$ and $Z^*$ are several orders of magnitude lower than $M$. For the case at hand $\kappa a = 0.1$, $\lambda_B = 0.72 \text{ nm}$, $d = 2.5 \text{ nm}$, $\eta = 10^{-4}$ are kept fixed, the colloidal radius changes from 20 to 140 nm.
2.5 Summary

So far we have formulated the Poisson-Boltzmann theory which describes the behavior of charged colloidal suspensions satisfactory. To avoid computational complications originating from the many-body character of the problem we subsequently employed the Wigner-Seitz cell approach. We also made an attempt to unambiguously introduce fundamental concepts of colloidal physics - charge renormalization and regulation - and applied the discussed theory to a hard-core macroion in an ionic solution. In the next chapter we will try to extend the Poisson-Boltzmann theory to the case of POM shells.
3 Application of the Poisson-Boltzmann theory to POM shells

Polyoxometalate shells do not have a hard-core and thus cannot be seen as "ordinary" colloidal particles we have considered so far. However our goal is to study electrostatics of the shells, and for this purpose the theory describing charged colloids is undoubtedly applicable. We again encounter the Poisson-Boltzmann equation with the only difference that it has to be solved inside the ball which the shell encloses as well.

3.1 Wigner-Seitz cell model for a POM shell

We will surround an individual POM shell by a spherical Wigner-Seitz cell and formulate a boundary value problem for it. Recall that it is sufficient to solve the Poisson-Boltzmann equation just for one cell since all of them are identical. The only small yet crucial difference from the already discussed case is that instead of an "ordinary" colloid we have a hollow one. Put differently, we need to solve the problem of a charged polyion without its interior. Let us see how the absence of the colloidal core affects the boundary value problem (34) formulated in (2.4).

For a negatively charged shell of radius $a$ and total charge $-Ze$ homogeneously distributed over its surface the charge density reads

$$\sigma = -\frac{Ze}{4\pi a^2} \delta(r - a).$$

(36)

It follows from the Poisson equation and Gauss’ law that

$$\phi'(a^+) - \phi'(a^-) = \frac{Z\lambda B}{a^2},$$

(37)

with $-\phi'(a^+)$ and $\phi'(a^-)$ proportional to the electric field strengths just outside and inside the POM shell surface, respectively.

We can now reformulate the boundary value problem (20) for the case of the charged thin spherical shell:

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \frac{\partial}{\partial r} \phi(r) \right] = \kappa^2 \sinh \phi(r);$$

(38)

$$\phi'(a^+) - \phi'(a^-) = \frac{Z\lambda B}{a^2};$$

$$\phi'(R) = \phi'(0) = 0,$$

where we assumed that the center of the POM sphere is in the origin. Finally, we include the charge regulation mechanism, just like we did in section (2.4), which means $Z$ in (38) has to be calculated according to (31):

$$Z = \frac{M}{1 + \frac{M}{K} \exp[-\phi(a)]}.$$

The set of coupled differential equations (38) tells us that the numerical procedure has to be modified. Now we need to find two branches of the electrostatic potential, one inside
the shell another outside. The former has the slope equal zero in the geometrical center of the superstructure (which is dictated by the symmetry of the charge distribution within the virtual cell), the latter is flat at the Wigner-Seitz cell boundary (thus ensuring the charge neutrality condition).

We employ the assumptions discussed in detail in the previous chapters, namely, (i) the solvent is treated as an homogeneous continuum characterized by the Bjerrum length \( \lambda_B \) and the Debye length \( \lambda_D \), (ii) microions are replaced by their average density profiles, \( \rho_{\pm}(r) \), (iii) many-body, image charge, hydrodynamic coupling effects are ignored.

To give a rigorous description of a suspension, as close to realistic as possible, one has to avoid the simplifications listed above. But tracing individual microions or replacing the continuous polar solvents by hard sphere molecules with permanent dipoles make numerical work virtually impossible because of expensive, time-consuming computations. For this reason we did not attempt to include solvent granularity and hard-sphere structure of microions in our model.

3.2 Numerical studies

In this section we will discuss various results obtained from the numerical studies of POM shells\(^{11}\). Where possible, we will draw parallels with the boundary problem for an ordinary hard-core colloid and emphasize major differences that were noticed.

We consider \( N_p \) POM monomers of diameter \( d \) in a macroscopic volume \( V \), such that

\[
\eta = \frac{\pi d^3}{6 V} N_p. \tag{39}
\]

Following the experiments we presume that the POMs can aggregate into \( N_s \) identical POM shells of radius \( a \), where each shell consists of \( n \) monomers. Describing the system of shells within the cell model (with a cell radius \( R \) and cell volume \( V_c = \frac{4}{3} \pi R^3 \)), we calculate for a given thermodynamic state the optimal values of \( N_s \) and \( a \). We assume here that all POM molecules take part in the shell formation, \( i.e. \) there are no free POMs floating around.

3.2.1 Electrostatic potential

We now proceed to calculate the radius of the Wigner-Seitz cell to be chosen. Assuming that monomers are on the shell surface, we find from geometrical reasoning the following relation:

\[
\alpha \cdot 4\pi a^2 = n \cdot \pi \left( \frac{d}{2} \right)^2, \tag{40}
\]

where we included the factor of \( \alpha < 1 \) which stands for the fraction of the total area of the POM shell surface covered by the monomers. For the case of the so called square packing each POM molecule has 4 neighbors and the corresponding \( \alpha = 0.785 \). If the number of neighbors is 6, which corresponds to hexagonal packing, \( \alpha = 0.91 \). We assume that the monomers are packed in the hexagonal manner. Together with \( N_p = nN_s \) we can write

\[
a^2 = \frac{d^2}{16\alpha N_s} = \frac{d^2}{16\alpha N_s} V \frac{\eta}{V_0} = \frac{d^2 \eta}{16\alpha V_0} \frac{4\pi R^3}{3} = \frac{d^2 \eta}{16\alpha \pi d^3} \frac{6}{3} = \frac{1}{2} \frac{R^3}{\alpha d \eta},
\]

\(^{11}\)we will be considering the shells consisting of \( \text{Mo}_72\text{Fe}_{30} \) monomers
Figure 10: A typical solution of the POM shell boundary value problem (38) under low salinity condition for a system of $\eta = 10^{-4}, \lambda_B = 0.72 \text{ nm}, M \approx 3 \cdot 10^4, \kappa a \approx 0.03, K = 5 \cdot 10^{-5} \text{ mol/l}, \rho_s = 10^{-7} \text{ mol/l}$. The highest absolute value of the potential is at the surface of the superstructure. Note that the slopes in the center of the shell and at the Wigner-Seitz cell boundary vanish.

such that the radius of the cell must satisfy

$$R = \left(\frac{2\alpha a^2 d}{\eta}\right)^{1/3}. \tag{41}$$

For fixed $\eta$ and $d$ this relates the cell and the shell sizes.

We modify the numerical scheme shooting now from the cell boundary with precisely zero slope and fit the initial guess $\phi_R$ such that we finish in the center of the POM superstructure with almost perfectly flat potential (the derivative $\phi'(0)$ is determined by the tolerance threshold which we set to be equal to $10^{-6}$).

In fig.10 such a dimensionless electrostatic potential satisfying (38) is plotted. We presume the radius of the shell $a = 20 \text{ nm}$. The diameter of a single POM $Mo_{72}Fe_{30}$ is $d = 2.5 \text{ nm}$, the number of dissociable groups on the surface of each monomer is $M_1 = 30$, such that the maximum number of ionisable charges of the shell is (just like in (35) but with $\alpha = 0.91$ included)

$$M = nM_1 = \frac{16\alpha a^2}{d^2}M_1. \tag{42}$$

We assume the ionic strength is very low, $\rho_s = 10^{-7} \text{ mol/l}$, $\lambda_B$ is that of water, 0.72 nm, the dissociation constant $K = 5 \cdot 10^{-5} \text{ mol/l}$, the packing fraction of POM monomers $\eta = 10^{-4}$ such that $R/a \approx 12.8$ as follows from (41). The values of the parameters listed
Figure 11: The electrostatic potentials for the values of $\kappa a = 0.6$ and $0.1$ (a) and the corresponding microionic and charge distributions for $\kappa a = 0.6$ (b). The parameters of the system are $\lambda_B = 0.72 \text{ nm}$, $K = 5 \cdot 10^{-5} \text{ mol/l}$, $a = 50 \text{ nm}$, $R/a = 3$. Top graph (a): the curve depicting the potential shifts up as $\kappa a$ increases from 0.1 to 0.6 - stronger screening yields smaller absolute value of the potential. Bottom (b): we recognize the high salinity regime - non-negligible fraction of counterions can be found even near the shell surface.
Figure 12: \( \tanh \phi(r) \) has to be close to the unity at the cell boundary at any instant of time in order to respect the low salt concentration condition, which is crucial for POM shells formation.

above are in accord with those used in the experimental setups of [16] and we take them as a reference point for our studies.

Observe that the potential plotted in fig.10 has a long nearly flat tail in the outer part of the cell. In general this poses computational problems like high sensitivity of convergence of the iterative procedure to the value of the initial guess \( \phi_R \).

For demonstrative purposes we plot in fig.11(a) two more solutions of the Poisson-Boltzmann boundary value problem (38) for a smaller cell radius, \( R = 3a \). We subsequently depict the (dimensionless) charge and co-/counterionic density profiles in fig.11(b) for \( \kappa a = 0.6 \). Although the curves in fig.11(a) are visually similar, the regimes they describe are quite different: the ionic strength of the solution for \( \kappa a = 0.6 \) is much higher. Consequently a substantial fraction of coions can be found even in the close vicinity of the like-charged shell surface, whereas for \( \kappa a = 0.1 \) the lines depicting the counterionic and charge densities (not plotted) nearly coincide.

We emphasize that we are preoccupied to keep the salinity low as this is reported to be the crucial condition for the POM shell formation. Demanding that there are almost no coions inside the Wigner-Seitz cell and that their fraction is negligibly small even at the cell boundary, we will formulate the criterion of low ionic strength as follows:

\[
\frac{\rho_+(R) - \rho_-(R)}{\rho_+(R) + \rho_-(R)} = -\tanh \phi(R) \simeq 1.
\]

In fig.12 we plot \( \tanh \phi(r) \) outside the shell for the potential presented in fig.10. This curve tells us that the microionic cloud inside the Wigner-Seitz cell consists almost exclusively
3.2.2 Regularized and renormalized charges

Once we have the electrostatic potential we can proceed to study the dependence of regulated and renormalized charges of a POM superstructure on its ionisable charge $M$. Assume the monomers are packed on the shell in a hexagonal manner, covering 91% of its surface, and presume the radius of the smallest superstructure to be $a = 20$ nm [16]. Starting with this smallest shell and iteratively increasing its radius we can easily find its bare charge just like we did it in (42) and calculate the renormalized charge according to Trizac’s prescription (24). For computational convenience we initially choose the ratio $\rho_s/K \sim 1$ and keep $\kappa a = 0.1$ fixed. Surrounding the shells by spherical Wigner-Seitz cells we numerically solve the boundary value problem (38). From fig.13, where we plot the dependence of the structural and the effective charges on the ionisable charge, we read off how important it is to account for the effects of regulation and renormalization: $Z_{\text{bare}}$ can be significantly larger than $Z^*$ and both are orders of magnitude smaller than $M$.

We further ask ourselves the following question. How does the replacement of the colloidal core with some solvent and microions influence the structural and effective charges? To elucidate this we consider a colloidal particle and a POM shell with absolutely identical geometrical and chemical characteristics and assume these samples are placed into the same bath. We solve (34) and (38) for the colloid and the POM shell, respectively, and use (24)
Figure 14: The structural and the effective charges (a) and the electrostatic potentials (b) of a hard-core colloid and of the same colloid without its interior (≡ POM shell) which are placed in the same reservoir. The parameters of the system are $\kappa a = 0.1$ fixed, colloidal/shell radius changes from 20 to 140 nm, $\lambda_B = 0.72$ nm, $\eta = 10^{-4}$, $K = 1.4 \cdot 10^{-6}$ mol/l. Top graph (a): observe that the angle formed by the curves which represent colloidal charges fits inside the one formed by those of a POM shell. Bottom (b): the hollow shell ($a = 140$ nm) is filled with water and microions in contrast to the colloidal hard-core. This yields lower absolute values of the potentials outside the POM sphere (compared to those of the corresponding colloid).
Figure 15: The dependence of $Z_{bare}$ and $Z^*$ of the POM shell on the ionisable charge $M$ for two various values of the packing fraction (a) and for two salt concentrations. Here $a = 20$ nm fixed, $\lambda_B = 0.72$ nm, $\kappa a = 0.1$, $K = 1.4 \cdot 10^{-6}$ mol/l. Top graph (a): the pattern formed by two curves representing $Z$ and $Z^*$ shifts towards lower values as we make the suspension denser ($\rho_s = 1.38 \cdot 10^{-6}$ mol/l). Bottom (b): the same trend is noticed as we increase the salt concentration from $\rho_s = 1.38 \cdot 10^{-8}$ to $\rho_s = 1.38 \cdot 10^{-6}$ mol/l.
to calculate the renormalized charges in both cases. The resulting graphs are presented in fig.14. As we can see all four charges are different - here one has to appreciate the difference in physical quantities the presence of microions inside of a polion may lead to. Conversely, the discrepancy between experimentally measured and theoretically predicted charges can possibly indicate the fact that the charged object under investigation might have hollow clusters underneath its surface.

As one can see from fig.14(b), the curve depicting the (negative) electrostatic potential around the colloid lies below the one that represents the $\phi$ in the outer subspace of the POM shell. If one now recalls the expression for the structural charge (31) it becomes clear why $Z_{\text{POMshell}}$ is larger than $Z_{\text{colloid}}$ (fig.14(a)).

The situation with renormalized charges is not so transparent. But we established that the effective charge of a hollow object with ionisable sites homogeneously distributed on a spherical shell of vanishing thickness is clearly smaller than that of the corresponding hard-core ball, although its bare charge may be significantly larger than the one of the colloid.

We are further interested in the dependence of $Z$ and $Z^*$ on the packing fraction. Consider a very dilute suspension we are currently working with ($\eta = 10^{-4}$) and a denser one of $\eta = 10^{-2}$. The radius of the Wigner-Seitz cell corresponding to the lower packing fraction is approximately three times bigger. To make the numerical task lighter we keep the radius of the shell constant and just vary the number of ionizable sites $M$. The results of the computation of $Z$ and $Z^*$ are plotted in fig.15(a). We can conclude that the curves representing both structural and renormalized charges shift upwards, insignificantly though, as $\eta$ decreases.
In a similar manner we study the charges $Z$ and $Z^*$ for various salt concentrations, say, $\rho_s \sim 10^{-8}$ and $\rho_s \sim 10^{-6}$ mol/l. As we add salt more co- and counterions are present in the suspension. The absolute value of oppositely charged cloud surrounding the colloid increases thus reinforcing the screening effect. We therefore predict that the effective charge $Z^*$ will be lowered. Moreover, stronger electrostatic interaction of the colloid with its double layer favors adsorption of counterions to the shell which in turn leads to smaller structural charges $Z$, and this is indeed what numerical studies confirmed. The results are presented in fig.15(b).

Our next interest is to get an idea of how bare and effective charges behave if we increase the packing fraction of POM monomers (see fig.16). One can see that both $Z$ and $Z^*$ are lowered, in the investigated range of $\eta$.

Poisson-Boltzmann cell model has not yet been applied to hollow spherical particles in ionic solutions. Therefore the effect of the absence of the hard-core on physical quantities may be a possible interesting direction of research.

### 3.2.3 Free energy and the equilibrium size of a shell in various solvents

After having discussed structural and effective charges, we insert the solution of (38) into the grand potential (33) to obtain the minimal grand potential of a single cell:

$$\beta \Omega = 4 \pi \rho_s \int_0^R dr r^2 \{ \phi(\rho) \sinh \phi(\rho) - 2 \cosh \phi(\rho) \} + \frac{Z}{2} \phi(a) - M \ln \left[ 1 + \frac{K}{\rho_s} \exp \left[ \phi(a) \right] \right],$$

which, to remind, includes the electrostatic and charge regulation contributions to the free energy of a single Wigner-Seitz cell.

Assume now that there are $N_s$ identical shells. To obtain the free energy of this system we therefore have to take $N_s$ times the free energy of a single shell:

$$F_{reg/st} = N_s \Omega.$$ (43)

Second, we take into account the ideal gas contribution:

$$F_{id} = N_s k_B T \left( \ln N_s \frac{d^3}{V} - 1 \right),$$ (44)

where an irrelevant constant is ignored. Finally, we also add the cohesive bond energy term which competes with electrostatic repulsions between POM monomers thus ensuring stability of the shells:

$$F_{bond} = N_s E.$$ (45)

Note, the $E$ used here stands for the energy of the hydrogen bonds linking the POM monomers on the shell surface\(^{12}\). This energy can be written as follows:

$$\beta E = -\gamma a^2 + \beta E_1 \frac{a}{d} + \beta E_0,$$ (46)

\(^{12}\)this energy should not be confused with the ionisation free energy in the section on charge regulation (2.4)! The latter will not show up later in the script.
with $\gamma$ the surface tension. The term $\sim a^2$ gives the major contribution to (46) and comprises the energy of all the bonds between the POM molecules on the shell surface in the absence of defects. However, it is known from Euler’s theorem \[26\] that there must be at least 12 monomers on a hexagonally packed spherical surface that have 5 rather than 6 neighbors. This results in 12 missing bonds on each shell and explains the origin of $\beta E_0$ correction in (46). There can also be other types of defects, like scars \[27\], which can give rise to a contribution to the bond energy linear in $a$. For this reason we included such a term in (46) with energy $\beta E_1$.

We can now write down the total free energy of the system of $N_s$ POM shells. It is an extensive quantity which consists of the three pieces (43) - (46):

$$ F = F^\text{reg}_{e/st} + F_{id} + F_{\text{bond}}. $$

(47)

Rather than working with the expression (47), it is more physically meaningful to re-express $F$ in terms of the free energy per individual POM monomer: $\beta F = N_p f_1$, with

$$ f_1 = \dfrac{\beta F}{N_p} = \dfrac{\beta F d^3}{V} \cdot \dfrac{V}{N_p \cdot \frac{4}{3} \pi \left(\frac{d}{2}\right)^3} \cdot \pi/6 = \dfrac{\pi/6}{\eta} \cdot \dfrac{\beta F d^3}{V} = \dfrac{\beta F}{\eta} \cdot \dfrac{N_s d^3}{V}. $$

Let us define

$$ \lambda \equiv N_s \dfrac{d^3}{V} = \dfrac{3\eta}{8\pi\alpha} \left(\dfrac{d}{a}\right)^2, $$

(48)

with which $f_1$ may be written as

$$ f_1 = \dfrac{\pi\lambda}{6\eta} \left\{ \beta \Omega + \ln \lambda - 1 + \beta E \right\} = \dfrac{1}{16\alpha} \left(\dfrac{d}{a}\right)^2 \left\{ \beta \Omega + \ln \lambda - 1 + \beta E \right\}, $$

(49)

with $\beta \Omega$ given by (33) and $\beta E$ by (46). As we will be interested in equilibrium sizes of POM shells we will have to minimize this energy $f_1$ w.r.t. $a$:

$$ \left. \frac{\partial f_1}{\partial a} \right|_{a=a_{\text{min}}} = 0. $$

Here we can point out the irrelevance of $(-\gamma a^2)$ in (46) for such studies. Indeed, upon the substitution of (46) in (49),

$$ f_1 = \dfrac{1}{16\alpha} \left(\dfrac{d}{a}\right)^2 \left\{ \beta \Omega + \ln \lambda - 1 + \beta E_0 + \beta E_1 a \dfrac{a}{d} - \gamma a^2 \right\}, $$

(50)

the presence of this quadratic in $a$ term yields $(-\gamma d^2/(16\alpha))$ - the constant which does not affect the minimum location. This is why the missing bonds (and hence $\beta E_0$ and $\beta E_1$ in (46)) are of primary interest for the explanation of the stability of POM shells. We can therefore reduce (46) to the following expression:

$$ \beta E = \beta E_1 a \dfrac{a}{d} + \beta E_0. $$

(51)
Figure 17: The dependence of the free energy per POM monomer $f_1$ on the radius of the superstructure. The parameters of the system are $\lambda_B = 0.72 \text{ nm}$, $\eta = 10^{-4}$, $\kappa a = 0.027$, $K = 5 \cdot 10^{-5} \text{ mol/l}$, $\beta E_0 = 600$. Stable POM shells of $a_{\min} = 30.5 \text{ nm}$ are expected to be formed. We see the minimum is quite shallow, $\sim 0.1 \, kT$ per POM if $a$ varies from $a_{\min}$ to $2a_{\min}$ in a single shell, which is consistent with the fact that the formation of shells is very slow [18].
Figure 18: The equilibrium size of POM shells vs. $1/\varepsilon$ of solvents for several values of the missing bond energy (with $\beta E_1 = 0$). Here $\eta = 10^{-4}$, $\kappa a = 0.027$, $K = 5 \cdot 10^{-5}$ mol/l.

The immediate conclusion is that the values of $\beta E_0$ are one order of magnitude higher than expected.

Our ultimate goal is to try to explain the experimental results of [16]. Because the ideal (44) and the electrostatic (43) terms are quite well defined they cannot be manipulated and fitted and hence we can only tune $\beta E$ in (51) in attempts to achieve a good correspondence with fig.4. As scar-like defects were not observed on POM shell surfaces, we initially assumed $\beta E_1 \equiv 0$.

Numerical studies of (49) show that for some values of $\beta E_0$ the free energy $f_1$ develops a minimum as a function of $a$. In fig.17 we plot such a concave curve for $\beta E = \beta E_0 = 600$, with the minimum located at $a_{\text{min}} = 30.5$ nm. As the minimum of the free energy corresponds to the equilibrium state of the system, one can hence expect that superstructures of the radius 30.5 nm will self-assemble from the reservoir with suspended monomers, for these parameters.

In order to achieve an agreement with the experiment we calculate a number of curves like those in fig.17 and plot their minima locations (i.e. radii of the POM shells) vs. $1/\varepsilon$ of the solvents. The resulting line is compared with that presented in fig.4, and in case we want a better fit the value of the missing cohesive bond energy $\beta E_0$ is changed accordingly and the procedure is repeated.

Such studies showed that a satisfactory fit can only be achieved provided that unreasonably large values of $\beta E_0 \approx 10^3$ are chosen (see fig.18). Given that according to Euler’s theorem there are 12 missing hydrogen bonds on a POM shell surface, we conclude that the energy of a single bond should be comparable to $100 \, kT$. This is one order higher than the well-established strength of this type of binding [28].
Figure 19: The equilibrium size of POM shells vs. $1/\varepsilon$ of solvents for several values of $K$ (a) and $M_1$ (b). Here $\eta = 10^{-4}$, $\kappa a = 0.027$. Top graph (a): the size of the shell is not very sensitive to variations of the dissociation constant ($M_1 = 30$). Bottom (b): the dependence of the shell size on the number of ionisable surface groups is weak ($K = 5 \cdot 10^{-5}$ mol/l).
Figure 20: The equilibrium size of POM shells vs. $1/\varepsilon$ of solvents for several values of $\beta E_1$ and $\beta E_0$. Here $\eta = 10^{-4}$, $\kappa a = 0.027$, $M_1 = 30$, $K = 5 \cdot 10^{-5}$ mol/l. Top graph (a): the lines obtained without the linear correction fall under the one found in experiments. For the best fit line $\beta E_0 = 850$, $\beta E_1 = 15$. Bottom (b): adding the term linear in $a$ can make the fit better.
In attempts to improve the correspondence with the experiment and to approach the realistic value of the binding energy we explored a broad range of the involved parameters. In particular, we varied the dissociation constant $K$ and the number of ionisable sites on each POM molecule $M_1$. It turned out that the location of the free energy (49) minimum is not very sensitive to these variations (see fig.19(a),(b)) and that the strength of the hydrogen bond still remains way too big.

Although one cannot say the fits we present in fig.18 and fig.19 are bad, one can see that the slopes of our calculated lines still fall under the experimental one. Variations of the system parameters result in insignificant parallel shifts, which does not fix the slope. We therefore decided to add a term growing as the shell expands in order to compensate for this discrepancy and restored $\beta E_1 > 0$ in (51).

In fig.20(a) we plot the best fit curve with $\beta E_1 = 15$ and $\beta E_0 = 850$. Although for the case of POM shells there are no physical grounds for the presence of the linear correction in (51), the correspondence with the experiment is better than if we choose $\beta E_1 = 0$ and $\beta E_0 = 1000$. For demonstrative purposes we also plot several curves with other values of $\beta E_1$ and $\beta E_0$ in fig.20(b). Smaller, compared to 15, values of $\beta E_1$ yield undershoots, larger lead to overshoots.

Summarizing the results, we can say that (i) The value of $\beta E_0 = 850$ corresponds to the energy of a single hydrogen bond $\approx 70$ kT, which is too big to be acceptable. (ii) The linear correction in (51), opposite to expectations, does not vanish. It appears that the parameters we have to choose in order to achieve a satisfactory correspondence with the experiments do not seem to be reasonable. We believe we have properly accounted for the ideal (44) and the electrostatic (43) pieces of the free energy and therefore conclude that perhaps yet unknown physical contribution(s) should be included in (49) to explain stability of POM shells rigorously and consistently. Alternatively, there could be many more (by a factor of about 10) than 12 defects in the hexagonal packing of the monomers on the shell surface.

### 3.2.4 Equilibrium size dependence on other parameters of the system

Even though we have established that most likely we are not aware of some peculiar physics of self-assembly, we still can study the qualitative behavior of POM shells. We would first like to find out how the location of the free energy minimum is affected if we go from a dilute suspension to a denser increasing the packing fraction of POM monomers. From fig.21(a), where we plot $f_1$ for $\eta = 10^{-4}$ and $\eta = 10^{-3}$, we see that $a_{\min}$ shifts towards higher values of $a$ with increasing $\eta$. Hence we can conclude that higher density of monomers favors larger shell sizes.

We further calculate the equilibrium size of the superstructure for various values of packing fractions keeping other parameters of the system fixed. On a logarithmic scale we plot the resulting curve (fig.21(b)) and point out that this dependence is monotonous until $\eta$ approaches 0.01. If we go to higher packing fractions shells rapidly collapse which means we have a fluid (or perhaps a crystal) of POM monomers.

We now consciously violate the low salinity constraint and inject more microions into the system to investigate their impact on the free energy minimum. This dependence is plotted in fig.22(a). One can notice a positive correlation between the salt concentration and the equilibrium size of the superstructure. It seems that for $\rho_s > 10^{-5}$ mol/l the minimum shifts to infinite radius, which means that under high ionic strength POM shells are not formed
Figure 21: The free energy $f_1$ (a) and the dependence of the equilibrium size of the POM shell on the packing fraction of the monomers (b). Here $\lambda_B = 0.72$ nm, $K = 5 \cdot 10^{-5}$ mol/l, $\rho_s = 10^{-7}$ mol/l, $\beta E_0 = 850$, $\beta E_1 = 15$. Top graph (a): we plot $f_1$ vs. $a$ for two various packing fractions. As $\eta$ increases by one order of magnitude the location of the minimum shifts along the x-axis from $a_{\text{min}} = 47.4$ nm to $a_{\text{min}} = 55.8$ nm. Bottom (b): the equilibrium size of the superstructure continuously and steadily grows as the monomer packing fraction increases until $\eta$ approaches 0.01. If we further immerse POMs the shell size rapidly decreases.
Figure 22: The free energy per POM molecule vs. the radius of the shell (a) and the equilibrium POM shell size dependence on the salt concentration (b). Here $\lambda_B = 0.72$ nm, $K = 5 \cdot 10^{-5}$ mol/l, $\eta = 10^{-4}$, $\beta E_0 = 850$, $\beta E_1 = 15$. Top graph (a): appreciate the dynamics: for lower salt concentrations monomers tend to self-aggregate in structures of smaller size. For example, the top curve has a minimum at $a = 60.4$, the middle at $a = 55.0$, the bottom one at $a = 47.4$ nm. Bottom (b): the equilibrium size of the superstructure continuously and steadily grows as the salt concentration increases until the minimum on the free energy disappears for some value of $\rho_s$, at which shells are not formed anymore.
anymore and instead planar structures could be expected.

3.2.5 DLVO potential. POM shell fluid or crystal?

In (1.1.3) we discussed the celebrated DLVO potential which governs repulsive interactions between charged bodies in ionic solutions. For high surface potentials this expression is still valid in the outer part of the Wigner-Seitz cell, provided that the bare charge \( Z \) in (7) is replaced with the renormalized one \( Z^* \). Let us estimate the strength of the interaction between two neighboring POM shells, assuming that two Wigner-Seitz spheres they are confined to touch each other, \( i.e. \) the distance separating their centers is \( r = 2R \):

\[
\beta V_{\text{shell-shell}}(r) = \lambda_B \left( \frac{Z^* e^{\kappa a}}{1 + \kappa a} \right)^2 \frac{e^{-\kappa r}}{r},
\]

(52)

where, as before in (22), at the cell boundary

\[
\tilde{\kappa}^2 = \kappa^2 \cosh \phi R.
\]

If \( \beta V_{DLVO}(2R) \) is weak (\( \ll 1 \)), two neighboring POM shells do not feel each other and freely float around in the solvent. We have a fluid of shells in this case. If on the other hand \( V_{DLVO}(2R) \) is bigger than unity one can expect a shell crystal with the phase transition occurring at \( \beta V_{DLVO}(2R) \approx 1 \).

In the usual manner we go to dimensionless quantities introducing \( x = r/a \) and rewrite the expression (52) as follows:

\[
\beta V_{\text{shell-shell}}(ax) = \frac{\lambda_B}{a} \left( \frac{Z^* e^{\kappa a}}{1 + \kappa a} \right)^2 \frac{e^{-\kappa ax}}{x}.
\]

(53)

For our touching shells \( x = 2R/a \). For each pair of values of \( \eta \) and the corresponding \( a_{min} \) plotted in fig.21(b) we calculate \( \beta V_{\text{shell-shell}}(2R) \) using (53). The results presented in fig.23(a) suggest that the system is strongly interacting and hence is in the crystalline phase, for all packing fractions that we studied. We subsequently used another criterion of liquid crystallization to verify this conclusion and calculated the \( \Gamma \)-parameter introduced in [29], which for our case reads

\[
\Gamma \equiv \beta V_{\text{shell-shell}}(\rho^{-1/3}) \left( 1 + k + k^2/2 \right),
\]

(54)

with \( \rho \) the number density of POM shells and \( k = \tilde{\kappa} \rho^{-1/3} \). According to point-Yukawa simulations performed in [29], crystallization occurs if \( \Gamma > 106 \). From fig.23(b) one reads off that this is clearly the case for packing fractions smaller than \( \eta \sim 10^{-3} \) - the system is strongly interacting which is characteristic for crystalline order. This is however not what was observed experimentally, and we therefore conclude that more detailed studies of self-assembly of polyoxometalates should be done in the future.
Figure 23: The inter-shell potential (a) is strong which suggests that the system is in the crystalline state. The coupling parameter $\Gamma$ (b) is bigger than 106 for packing fractions smaller than $\eta \sim 10^{-3}$. Here $\lambda_B = 0.72$ nm, $K = 5 \cdot 10^{-5}$ mol/l, $\rho_s = 10^{-7}$ mol/l, $\beta E_0 = 850$, $\beta E_1 = 15$. 

46
3.3 Summary

In this conclusive chapter we extended Poisson-Boltzmann theory for charged colloids in ionic solutions to the case of hollow spherical particles. The crucial difference is that instead of a hard-core the space inside a thin shell is filled with solvent and microions, just like outside. We solved the nonlinear Poisson-Boltzmann equation within the framework of the Wigner-Seitz cell model taking into account charge regulation and renormalization mechanisms. Subsequently we applied the theory to polyoxometalate shells in attempts to explain their equilibrium size dependence on the system parameters. It turned out that the bond energies we have to choose in order to achieve a satisfactory correspondence with the experiments are unreasonably high. Possible explanations to this result may originate from the presence of many more defects than expected or lie deep in obscure physics and chemistry of self-assembly of this system.
4 Conclusions and outlook

In this thesis we studied polyoxometalate shells in low ionic strength solutions by means of nonlinear Poisson-Boltzmann theory. Starting from the well known formulation of the Poisson-Boltzmann boundary value problem in a spherical cell (20), we briefly discussed suspensions of hard-core colloids and charge renormalization (2.3) and regulation (2.4) mechanisms. Subsequently in chapter 3 we extended the theory to treat hollow spherical particles, in all respects similar to ”ordinary” colloids apart from the absence of a hard-core which is replaced with an ionic solution. We solved the electrostatic problem (38), i.e. found two branches of the potential, and calculated the corresponding microionic distributions (fig.11). The structural and effective charges of a colloid and a geometrically and chemically identical POM shell were compared (fig.(14)).

Locating minima of the free energy (49) for various system parameters and matching them with the equilibrium sizes of POM shells synthesized experimentally was the major part of the numerical work. We initially assumed there are precisely 12 (as suggested by Euler’s theorem) missing molecules on each POM shell surface. It turned out that the calculated strength of inter-monomer binding is one order higher than that obtained from the experiments. In principle the discrepancy can be attributed to the presence of many more dislocations on shell surfaces. This would result in formation of scar-like defects. Assuming the latter exist, we again estimated the strength of the bonds between POM molecules on the surface of the sphere and found it is still too big, however the fit (fig.20(a)) slightly improved.

Although we did not succeed to confirm the results of [16] using the approach suggested in (3.2.3), we pointed out possible explanations to the discrepancy with the experimental data: (i) there could be many more than 12 defects on each POM shell surface composed of thousands of monomers, and (ii) some aspects are missing from the theory of self-assembly of patchy particles.

If we talk about the directions of further research, it may be interesting to study electrostatics of particles with hollow clusters, pores or voids underneath their surfaces. Absence of the hard-core, as we established, may lead to differences in physical quantities. In future it is crucial that scientists elucidate the origin and construct quantitative description of anisotropic attractive forces encountered in self-assembly of polyoxometalates.
Acknowledgements

I thank my parents and my brother, and altogether we are endlessly thankful to the people who helped me along the way, in first turn to my Greek friend Dimitris. Thank you Ardavan, León, Stefanos and all other guys too.

It was a pleasure to work on this project together with René van Roij - an enthusiastic teacher and a very nice person. Many thanks to Henk van Beijeren, Frank Witte and Gerard Barkema who made it possible for me to study in Utrecht University and to the professors who taught me basics of theoretical physics.
References


