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Abrikossov, Alexei

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ALEXEI ABRIKOSSOV

Modelling anisotropic interactions in colloidal systems

Alexei Abrikossov

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Faculty opponent

Associate Professor Sofia Kantorovich, Computational Physics, Faculty of Physics, University of Vienna, Vienna, Austria

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Abstract

There has been an increased interest to design “smart materials” which can self-assemble into complex structures in accordance to external factors such as for example electromagnetic fields. By designing particles with directional interactions one is able to control how particles will interact with each other. By means of both Monte Carlo and Molecular Dynamics simulations we study the interactions of three distinct types of models namely the self-assembly of off-centered dipoles, the charged patchy particle model in multivalent electrolytes, and an all atom model of [3,3’-cobalt(III) bis(1.2-dicarbollide)] and its interaction with solvent. Besides this there is also a short discussion about the long-range anisotropic interactions and ways by which one can calculate them.

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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 **Self-assembly of spherical colloidal particles with off-centered magnetic dipoles**
Alexei I. Abrikosov, Stefano Sacanna, Albert P. Philipse and Per Linse
Soft Matter, **9**, 8904-8913 (2013)

II **Metallacarboranes are Nonclassical Surfactants. A Concerted Application of Experiments and Multi-Scale Modeling Provide a Molecular Picture of Their Aggregation in Solution**
Mariusz Uchman, Alexei I. Abrikosov and Mikael Lund, Martin Lepšík, Zdeněk Tošner, Pavel Matějíček
Manuscript

III **Steering Patchy Particles Using Multivalent Electrolytes**
Alexei I. Abrikosov, Mikael Lund
Submitted

IV **Direct summation of dipole-dipole interactions using the Wolf formalism**
Björn Stenqvist, Martin Trulsson, Alexei I. Abrikosov, Mikael Lund
J. Chem. Phys., **143**, 014109 (2015)

List of Contributions

I I planned and carried out the simulations and took active part in writing the text.

II I planned and carried out all the molecular dynamics simulations and wrote the related text.

III I took active part in writing the paper; performing simulations and analysing data.

IV I was responsible for the reaction field Monte Carlo simulations as well as writing and analyzing that part in the paper.

Contents

Populärvetenskaplig sammanfattning

Under den senaste tiden har det varit ganska populärt att studera smart materia som kan bilda nya strukturer beroende på externa förhållanden. Detta arbete är fokuserat på att studera hur man kan designa sådan materia. Med hjälp av dator simuleringar har vi modellerat partiklar med riktade interaktioner och studerat deras beteenden i bulk.

Förhoppningen är att om man kan få en modell som beskriver beteendet av partiklarna, så kan man ta reda på information om partiklarna som inte går eller är besvärligt att ta reda på med hjälp av experiment. Till exempel så är det näst intill omöjligt att ändra en partikels dipolmoment under ett experiment, men det är hur lätt som helst i en simulering. En annan fördel av att använda sig av simuleringar är att man kan få en inblick över hur individuella partiklar beter sig vilket för många experimentella system helt omöjligt.

Genom simuleringar kan vi prova olika parametrar, ändra partiklarnas form och ändra de externa förhållandena så vi systematisk kan studera vilka parametrar ansvarar för vad och till vilken nivå. Med hjälp av denna information kan experimentalister försöka få fram nya material som kanske kommer nytta mänskligheten i framtiden.

Chapter 1

Introduction

When I first learned about colloids, what surprised me the most was the sheer range of materials that are classified as colloids. Just a quick search will inlighten one, that such common tings like milk, paint, clouds, dust and whipped cream are all colloids. Thus one can deduce that colloidal materials were used and encountered by humans for the greater part our history. Today people have learned how to make custom made colloidal materials that can interact in a predictable fashion and serve a specific purpose. This thesis will describe some of the models and methods that can be used to study the interactions and phase behaviour of colloidal particles by the means of computer simulations.

Despite humanity's use of colloids throughout history, colloidal science did not really begin until the mid 19th century when Francesco Selmi performed systematic studies describing the first "pseudo-solutions" of silver chloride, Prussain blue and sulfur. Thomas Graham introduced the term *colloid* (meaning Glue in Greek) nearly 20 years later, noting that these types of particles deserve to be in a class of their own.[1]

So how do we define colloidal particles and what is so fascinating about them? A classical definition of a colloidal particle is that it is a particle roughly between 1 nm and 1 μm which is dispersed in a solvent and exhibits Brownian motion. The key word in that description is *dispersed*, colloidal particles are not solvated by the solvent but the mixture is still pseudo-stable. Faraday was one of the first to study this fenomenon by conducting experiments on colloidal sols[2] (solid particles dispersed in liquid) in the 1850s. Some of the mixtures were so stable that they are still on display in museums.[3]

A big leap in colloidal science came with the development of the DLVO theory, named after the authors of the pioneering publications of Derjaguin and Landau from the USSR[4] and Vervey and Overbeek from the Netherlands.[5] The theory describes the way the attractive van der Waals and repulsive electrostatic forces affect the aggregation and stability of colloidal particles.

This brings us to the custom made colloidal particles of today. These particles can be fine tuned to take on several shapes[6,7] (see Fig 1.1) and interact via isotropic or anisotropic interactions. Another helpful property of colloids is that their interactions can be tuned by for example altering salt concentration, temperature, pH and applying external electromagnetic fields.[1,8] Thanks to colloidal particles, it became possible to experimentally confirm theoretical models such as hard-spheres.[9] In return the use of computer simulations became well suited to study colloidal systems when the DLVO theory was not enough to describe the colloidal interactions.

In Paper I we describe the self-assembly of particles with an off centered dipole moment. In the paper we expanded the model used by Kantorovich et al.[10] to closer resemble the exerimental system studied by Saccana et al by the means of Monte Carlo simulations. In Paper II we study the an all atom model of the metallocarborane cluster [3,3′-cobalt(III)bis(1.2-dicarbolide)](-1 anion) using Molecular dynamcs to better understant its aggregation. In Paper III we study the effects of trivalent ions on the interaction of charged patchy particles as a means to understand the phase behaviour of proteins in multivalent electrolytes. In the last paper Paper IV we developed a new way of calculating the long range electostatic interactions by expanding the Wolf-method and comparing our results to some established schemes.

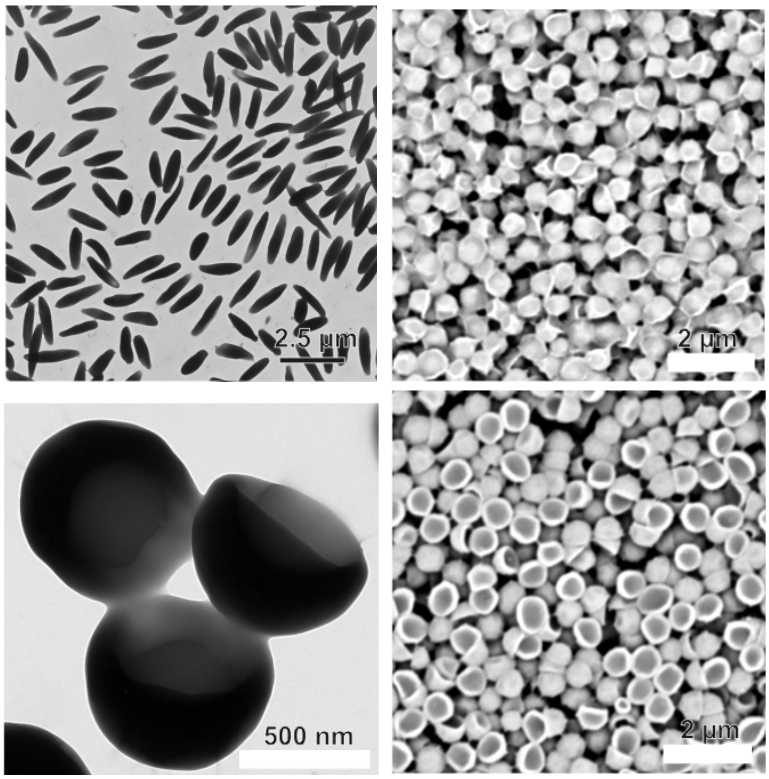

Figure 1.1: *Examples of the different shapes that modern day colloidal particles can be designed to have, curtosy of Dr. Jerome Crassous*[7]

Chapter 2

Statistical mechanics and computer simulations

2.1 Basics of statistical mechanics

The field of statistical mechanics is based on the fundamental postulate that in an isolated system all microscopic states are equally populated. This postulate enables us to use statistics and probabilities to determine macroscopic equilibrium properties of a system.[11] The definition of entropy:

$$S \equiv k \ln \Omega \tag{2.1}$$

is one of the main workhorses of statistical mechanics. Here Ω is the number of microscopic or quantum states and k is Boltzmann's constant, conventionally given to achieve a unit of measurement.

Statistical mechanics enables us to calculate macroscopic properties of a system using microscopic information. Imagine an isolated container of particles: which enteties describe the system? Well, we could say that the container has volume V, the number of particles in the container is N and the total energy inside the container is U. These are the *independent* variables describing the system and do not change, thus the total number of microscopic (quantum) states is.

$$\Omega = \Omega(U, V, N) \tag{2.2}$$

Now the pressure is defined as force per unit area. If we calculate the force from all the particles on the wall of the container it will wildly differ from instant to instant. What we experience on the macroscopical

level however is a time averaged force. Thus all we have to do is describe how all the particles in the container should move and calculate the time average force on the container to get the macroscopic properties we are looking for. Before computer simulations this was most often an impossible task. A solution to the problem was suggested by Gibbs via the *ensemble method*.[11] But what is an ensemble? Well, the ensemble is all the microscopic states defined by our independent variables. Instead of averaging over *time*, one averages over the different microscopic states thus obtaining the so called *ensemble* average. This approach uses another basic postulate of statistical mechanics namely, the ergodic hypothesis:

The infinite time average of any mechanical variable is equal to the ensemble average of the same variable with an infinite number of member systems in the ensemble.[11]

Without going into many more details about statistical mechanics, we mention that the ensemble method proved to be viable in analytically determining expresions for macroscopic properties. By using the ensemble method together with the first law of thermodynamics that describes the changes in energy dU,

$$dU = \delta\hat{Q} + \delta\hat{W} \tag{2.3}$$

Where $\delta\hat{Q}$ is heat transferred and $\delta\hat{W}$ is work done. One can determine the entropy S, pressure P, chemical potential μ and temperature T just by knowing the partition function $\Omega(U, V, N)$.

The ensemble used in the above example is the so called *microcanonical* ensemble and is sometimes impractcal to work with. Other ensembles are the canonical that uses N, V and T as the independent variables with

$$Q = \sum_i e^{-\frac{U_i}{kT}} \tag{2.4}$$

as its partition function describing the Helmholtz free energy

$$A = -kT \ln Q. \tag{2.5}$$

Another popular ensemble is the *isobaric-isothermal* ensemble where the pressure P and T are constant thus the partition function is

$$\Delta = \sum_i e^{\frac{-U_i}{kT}} \sum_j e^{\frac{-PV_j}{kT}} \tag{2.6}$$

with the Gibbs free energy

$$G = -kT \ln \Delta \tag{2.7}$$

and the grand canonical that uses μ, V and T with

$$\Xi = \sum_i e^{-\frac{U_i}{kT}} \sum_j e^{-\frac{N_j \mu}{kT}} \tag{2.8}$$

as the partition function describing the grand potential

$$\Lambda = -kT \ln \Xi. \tag{2.9}$$

2.2 Simulations

Unlike Gibbs we today have powerful computational tools to our disposal that can be used to calculate how particles propagate over time. Over the past 60 years computers have gradually become a household item and are everywhere from washing machines to smart phones. At the beginning they were big, so big in fact that they took up several rooms. Now how could scientists of the time walk past such an amazing piece of technology and leave it in the hands of the military[12]? Thus the famous Monte Carlo (MC) method was born.[13] The MC method makes use of computers ability to generate a large amount of (pseudo) random numbers and uses this as a means to perform calculations. When it comes to statistical mechanics is is quite easy to see that the MC method could be used to generate different micro states of an ensemble. The approach of using the more physical *time* propagation was also developed and got the name of Molecular dynamics (MD) and uses Newtons, equations of motion to propagate the system in time. Despite technological advances, the amount of particles that one can handle in a typical MD or MC simulation is still well below the number you would have in a macroscopic system with N in $\mathcal{O}(10^{20})$.

2.3 Periodic boundary conditions

In a simulation, the number of currently manageable particles, is still very small compared to the number of particles in a macroscopic system. Thus one faces the problem that a big percentage of particles interact with the wall of the simulation container. A way to minimize this effect without

actually increasing the number of particles in the calculation is to use *periodic boundary conditions* (PBC). In PBC replicas of the your simulation box are created in all directions, filling infinite space. In practice, however one ends up using *toroidal boundary conditions* where when a particle leaves the simulation box in one end it enters from the other. This enables us to find neighboring particles on the other side of the wall so to speak.

2.4 Metropolis Monte Carlo

Let us look at the Monte Carlo method in more detail. As stated above, the method utilizes pseudo random numbers to perform a statistical analysis of how a system behaves. Thus the method is used in a variety of fields for very different purposes. In astronomy you can for example calculate the probability of the formation of an earth like planet; in particle physics one can use the method to calculate the paths of the quarks and bosons after a nuclear collision; and in medicine one can use Monte Carlo to simulate the treatment of a radiology patient. One popular implementation of the algorithm used in statistical mechanical simulations is referred to as Metropolis Monte Carlo[14] which describes how particles explore a volume of space. Two main features of the Metropolis Monte Carlo are *importance sampling* and *detailed balance*.

Importance sampling is a term that describes the fact that you only need to sample in the region of space that you are interested in. Not that this is inherently necessary, but why should one take samples in Sweden instead of Egypt if you want to know the depth of the Nile.[15] In Metropolis Monte Carlo this is achieved by weighting the choice of a new state by a Boltzmann factor[15] which makes the simplest implementation of the method inherently perform calculations in the canonical ensemble.

Importance sampling goes hand in hand with detailed balance which states that the probability of being in the old state (o) and from there moving to a new state (n) has the same probability as being in the new state and then moving to the old state. This can be summarized by the following equation:[15]

$$N(o)P(Acc.o \to n) = N(n)P(Acc.n \to o) \tag{2.10}$$

Here $N(x)$ is the probability of being in a certain state and $P(Acc.)$ is the probability of accepting a specific move.

Thus a typical algorithm of a Metropolis Monte Carlo simulation is as follows,

i) Generate a new configuration by for example moving a particle in a random direction with a random displacement.

ii) Calculate the difference in energy between the new and old system $\Delta U = U_{new} - U_{old}$.

iii) If the energy decreases, accept the move. If the energy increases compare the Boltzmann weight $e^{-\frac{\Delta U}{kT}}$ to a uniform random number between 0 and 1. If the random number is less than $e^{-\frac{\Delta U}{kT}}$ accept the move, otherwise reject it.

iv) If the new configuration is accepted sample it otherwise sample the old configuration.

v) Go back to step (i)

In general, Monte Carlo is a robust technique for calculation of static equilibrium properties i.e. collecting ensemble averages but inherently lacks dynamics. Also, detailed balance is a condition that should be preserved (altought not always necessary). This can be tricky when one tries to enhance the sampling rate by for example introducing cluster moves like in Paper I.

2.5 Molecular dynamics

As described previously, the Molecular Dynamics method uses the forces exerted on the particles to move them for a small time interval using Newtons equations of motion.

$$\frac{d^2\boldsymbol{r}_i}{dt^2} = \frac{\boldsymbol{F}_i}{m_i}; \quad \frac{\boldsymbol{r}_i}{dt} = \boldsymbol{v}_i; \quad \frac{\boldsymbol{v}_i}{dt} = \frac{\boldsymbol{F}_i}{m_i} \tag{2.11}$$

The main engine of the MD calculation is the *integrator* that solves these equations numerically and propagates the system. The main condition for these integrators, is that the calculations should be reversible, meaning that starting a subsequent calculation in reverse should lead to the

initial configuration. There are several integrators but some of the popular ones are the Verlet algorithm and its derivatives velocity Verlet[16] and the Leap-frog[17] algorithms.

The Verlet algorithm is in essence a Taylor expansion of the particles coordinate around time t. This leads the method to not utilize the velocity of the particles in determination of the new positions, thus leading to the need to separately calculate the velocities from the trajectory. Which results in the differing accuracy of the two calculations.

$$\boldsymbol{r}(t+\Delta t) = 2\boldsymbol{r}(t) - \boldsymbol{r}(t-\Delta t) + \frac{\boldsymbol{F}(t)}{m}\Delta t^2 + \mathcal{O}(\Delta t^4) \tag{2.12}$$

$$\boldsymbol{v} = \frac{\boldsymbol{r}(t+\Delta t) - \boldsymbol{r}(t-\Delta t)}{2\Delta t} + \mathcal{O}(\Delta t^2) \tag{2.13}$$

Here and in the following equations, $\boldsymbol{r}$ is the position, v is the velosity, t is the time, Δt is the time step and $\boldsymbol{F}$ is the force on the particle.

The Leap-frog algorithm got its name because of how it uses positions $\boldsymbol{r}$ at time t and velocities v at time $t - \frac{1}{2}\Delta t$. The algorithm also uses the forces $\boldsymbol{F}(t)$ at time t to calculate how the velocities and positions should be updated.

$$\boldsymbol{v}(t+\frac{1}{2}\Delta t) = \boldsymbol{v}(t-\frac{1}{2}\Delta t) + \frac{\Delta t}{m}\boldsymbol{F}(t) \tag{2.14}$$

$$\boldsymbol{r}(t+\Delta t) = \boldsymbol{r}(t) + \Delta t\boldsymbol{v}(t+\frac{1}{2}\Delta t) \tag{2.15}$$

Note however that the velocities and positions are not calculated for the same time which can lead to problems in determining the total energy of the system.

Unlike the original Verlet algorithm that did not use velocities to update particle positions, the velocity Verlet algorithm was intentionally expanded to include the velocity in the calculation. The algorithm also has the advantage of having the velocities and the positions defined for the same time:

$$\boldsymbol{r}(t+\Delta t) = \boldsymbol{r}(t) + \Delta t\boldsymbol{v}(t) + \frac{\Delta t^2}{2m}\boldsymbol{F}(t) \tag{2.16}$$

$$\boldsymbol{v}(t+\Delta t) = \boldsymbol{v}(t) + \frac{\Delta t}{2}[\boldsymbol{F}(t) + \boldsymbol{F}(t+\Delta t)] \tag{2.17}$$

The drawback of the method is that the new velocities can only be computed after the new positions and new forces. Because the total energy of the system should be conserved when using these algorithms, MD calculations are inherently in the microcanonical ensemble (N,V,U). This makes using thermostats[18,19,20,21] and barostats[18,22,23] a common occurrence when using this method, since one is usually interested in the canonical or isotrem-isobar ensembles which resemble experimental systems. The main advantage of MD calculations, besides its ability to sample dynamic properties, is that the method is well suited for parallel computing. This feature enables one to compute much bigger systems than those that are calculated using typical MC methods.

Chapter 3

Intermolecular Interactions

If we look back at what was discussed in Chapter 2 and derive the expression for pressure from the partition function of an ideal system we get:

$$PV = NkT \tag{3.1}$$

also known as the ideal gas law.

This expression ignores that particles have size and can interact with each other. In the second half of the 19th century Johannes Diderik van der Waals derived an expression that (approximately) took this into account.[24]

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \tag{3.2}$$

In this equation V_m is the molar volume and a, b are the van der Waal parameters. Now how these extra parameters look depends in large part on the way the particles interact and in the following we will present common interaction potentials.

3.1 Hard-Sphere potential

One of the simplest ways to describe interactions between two particles is in the form of spheres that cannot overlap. The interaction potential becomes

$$u(r) = \begin{cases} 0 & \text{if } r \geq \sigma \\ \infty & \text{if } r < \sigma \end{cases} \tag{3.3}$$

where the potential $u(r)$ is zero if the particles do not overlap and infinity if they do. It is common to let r represent the center to center distance

between the particles and σ to describe the diamater and will in the following adhere to this.

3.2 Lennard-Jones potential

Unlike the Hard-Sphere potential, the Lennard-Jones (LJ) potential[25] has both a repulsive and an attractive term which is often a better description of how real particles interact. In the early works the potential was of the form,

$$u(r) = \frac{\lambda_n}{r^n} - \frac{\lambda_m}{r^m} \tag{3.4}$$

where λ_n and λ_m are positive, particle dependent numbers. The first term describes the repulsion between particles, the second attraction. Even in the early days of development, the attractive term has been linked to the dispersion energy, thus $m = 6$ became the standard value to use. The repulsion however is not linked to any specific theoretical value of n, but since $m = 6$ it became standard to use $n = 12$, sinse doing so provides a computational advantage. In its current form the potential is usually written:

$$u(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] \tag{3.5}$$

Where ϵ determines the maximum strength of the attraction.

3.3 Weeks-Chandler-Andersen potential

The Hard-Sphere potential is a discontinues model meaning there is a sharp transition between repulsion and no interaction. Lennard-Jones on the other hand has a smooth transition between repulsion and attraction but sometimes you want to separate attraction from repulsion. This is the idea behind the Weeks-Chandler-Andersen (WCA) potential.[26] The potential separates the repulsion and attraction of a pair potential (in our case in Paper III and in the original publication this was the LJ potential) into two separate parts so that one will have all the repulsion and the other all the attraction.

$$w(r) = u_0(r) + u(r) \tag{3.6}$$

Here $w(r)$ is the final potential while $u_0(r)$ is called the reference system pair potential that has all the repulsion and $u(r)$ is the perturbation potential that has all the attraction. There is an additional condition that $u_0(r) \to 0$ as $r \to \infty$ giving us:

$$u_0(r) = \begin{cases} 0 & \text{if } r \geq 2^{\frac{1}{6}}\sigma \\ w(r) + \epsilon & \text{if } r < 2^{\frac{1}{6}}\sigma \end{cases} \tag{3.7}$$

$$u(r) = \begin{cases} w(r) & \text{if } r \geq 2^{\frac{1}{6}}\sigma \\ -\epsilon & \text{if } r < 2^{\frac{1}{6}}\sigma \end{cases} \tag{3.8}$$

The ϵ in this case is a shift parameter and $2^{\frac{1}{6}}\sigma$ is where the minimum of the LJ potential is located. Thus in essence what the WCA potential does is to cut the LJ into two parts at its minimum and shifting the repulsive part up to zero at the cutoff giving us soft and purely repulsive potential that was used in Paper III.

3.4 Electrostatic interactions

Besides size exclusion and dispersion, particles may carry charge or a charge distribution. This can be described with varying degrees of accuracy, but in here we limit ourselves to charges and dipoles.

One of the fundamental laws of nature is Coulombs law that describes the force between two charges. For our purpose it is more beneficial to look at the potential,

$$u(r) = \frac{q_i q_j}{4\pi\epsilon_0\epsilon_r r_{ij}} \tag{3.9}$$

where q_i and q_j are charges and $\epsilon_0\epsilon_r$ the permittivity and r_{ij} is the distance between the charges.

The first correction to describe electrostatic anisotropy of a charge distribution is by means of the electric dipole moment,

$$\boldsymbol{\mu} = \sum_{k=1}^{N} q_k \boldsymbol{r}_k \tag{3.10}$$

Here q_k are the individual charges and $\boldsymbol{r}_k$ are their corresponding position vectors. In the case of only two charges, one positive and one negative, the dipole moment can be seen as a vector pointing from the negative charge to the positive. If one would scale the distance between the charges with $1/n$ and the charges with n, in the limit of n approaching infinity we get a point dipole moment. The point dipole is a mathematical abstraction but is nonetheless very useful to use in simulations, since one can describe

the point dipole moment as a vector alone. The potential between two dipoles is,

$$u(\boldsymbol{r}_{ij}, \boldsymbol{\mu}_i, \boldsymbol{\mu}_j) = -\frac{1}{4\pi\epsilon_0\epsilon_r}\left[3\frac{(\boldsymbol{\mu}_i \cdot \boldsymbol{r}_{ij})(\boldsymbol{\mu}_j \cdot \boldsymbol{r}_{ij})}{(r_{ij})^5} - \frac{\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j}{(r_{ij})^3}\right] \tag{3.11}$$

in this expression $\boldsymbol{r}_{ij}$ is the vector between dipole i and j, $\boldsymbol{\mu}_i$ and $\boldsymbol{\mu}_j$ are their corresponding dipole moments, r_{ij} is the scalar distance between them.

The main challenge of electrostatic interactions in computer simulations is their long ranged nature. The interactions decay as $1/r$ in the case of charge-charge interactions and $1/r^3$ in the case of dipole-dipole interactions. Specificaly, the problem that one faces is that the decay of electrostatic interactions is not fast enough to simply use a cut-off within the simulation box. Several methods to deal with this problem has been proposed over the years which is the purpose of the next section.

Reaction field

The method was developed to describe how a dipole interacts with its surrounding medium. This is done by placing a dipole in a cavity surrounded by an infinite medium defined by a dielectric constant, ϵ_r. By letting the dipole polarize the surrounding medium, the resulting polarization will in turn create an electric field which affects the dipole in the cavity, hence the name *Reaction Field*. As computer simulations became more widespread the method was included by Baker and Watts in their publication showing that the results achieved with the Reaction field method are more accurate than if one would just use a spherical cutoff.[27] The Reaction field method is a fast method sacling as $\mathcal{O}(N)$, with N being the number of charges in the system, and is easily implemented. However the methods greatest drawback is the need for a correct parametrization of the dielectric constant of the surrounding medium wich is not an easy task in all cases.

Ewald-summation

A widespread way of tackling the problem of long range electrostatics in computer simulations is to use the so-called Ewald-summation.[28] The method utilizes PBC and splits the system energy into a short range part which is calculated in real space and a long range part which is calculated

in reciprocal space. By doing so, one transforms the conditionally convergent system into two parts that are both absolute convergent. Because the method utilizes PBC it is viable for charge-neutral systems, something one should always be aware of. The method requires cutoff parameters in both real and reciprocal space, but the biggest drawback is the computational cost which scales as $\mathcal{O}(N^2)$ or $\mathcal{O}(N^{\frac{3}{2}})$ when optimized.

Wolf-method

It has been noticed that in dense systems the electrostatic interactions become effectively short ranged. Further observations gave insight that, if the total charge within a certain cutoff is exactly or near zero, one can calculate the energy using a simple pairwise truncated and shifted Coulomb potential without getting significant errors.[29] Thus Wolf et. al. proposed to use charge neutralization by placing a counter charge at the cutoff sphere as a means to utilize the shifted pair potential. The convergence using this approach was later improved upon by using a damping function, akin to the real-space part of the Ewald summation. The advantage of using the Wolf formalism instead of Ewald summation is that the computational cost of this method scales as $\mathcal{O}(N)$ which would allow for bigger simulations. In Paper IV we further expanded the formalism to describe dipolar interactions.

Chapter 4

Modeling

Modeling is simply a way of describing reality. A model can be complex or it can be simple, but what defines a good model? There is no single correct answer to this question, but here are some points that one should consider,

i) Does the model describe what we want it to describe?

ii) How well does it describe it?

iii) How sensitive is it to the change in details?

In this section we discuss the background behind the models used in Paper I to III.

4.1 The off-centered dipole

The dipolar particle (DP) as a model has been used in many studies and is a simple way to model for example ferro-fluids.[8] The model is a sum of two potentials: an isotropic short range (sr) potential plus the dipole-dipole (dd) potential.

$$u_{DP}(r) = u_{sr}(r) + u_{dd}(r) \tag{4.1}$$

In this model the dipole is positioned at the center of the particle. Now the dipole-dipole interaction is anisotropic but there is still rotational symetry in this model.

We now introduce an internal coordinate system for the particle, and place a dipole moment in the middle of that coordinate system pointing

in a random direction. We will get different particles, but since we can simply rotate these particles to get the same overall configuration, the particles become indistinguishable, see Fig 1a. While this may seem obvious and unnecessarily complicated, this separation in the treatment of the dipole by itself and of the particle by itself is important components in the model of the off-centered dipolar particle (ODP).[10,30]

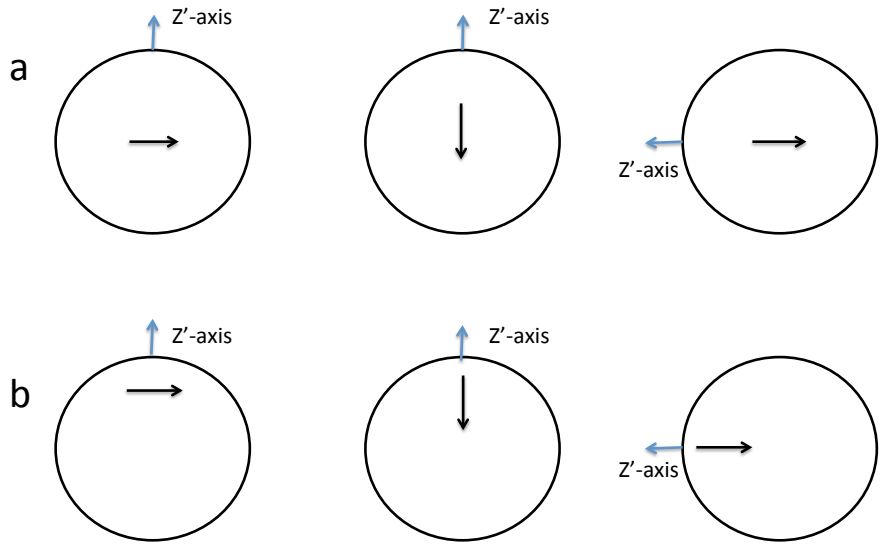

Figure 4.1: *A schematic representation of the (a) dipolar particle with a central dipole. No matter in which direction one places the dipole you can always rotate the particle to get the same configuration, (b) off-centered dipolar particle it is no longer possible to get the same configuration by simply rotating the particle.*

$$u_{ODP}(r_{sr}, r_{dd}) = u_{sr}(r_{sr}) + u_{dd}(r_{dd}) \tag{4.2}$$

Several things that happen when moving the dipole from the center of the particle towards the periphery:

i) There is less symmetry, see Fig 1b.

ii) The dipole-dipole distance may become shorter.

iii) Because of the short range repulsion, the particles can no longer rotate freely (at contact) to get the "best" dipole-dipole orientation.

iv) Because the dipoles are closer to the surface of the particle, one side of the particle will be preferred over the other.

All this only plays a significant role when the particles are in contact but that is sufficient to yield a completely different self-assembly than normal dipolar particles, as is shown by Kantorovich et al. and Paper I.

4.2 An all atom model

Another model considered in this work is the metallocarborane cluster [3,3'-cobalt(III)bis(1.2-dicarbolide)](-1 anion) also referred to as COSAN or $[CoD]^-$. We will refer to it as COSAN from here on, but the term $[CoD]^-$ is used in Paper II. The term COSAN comes from the shape of the molecule where the cobalt atom is sandwiched by two dicarbolide $nido - (C_2B_9H_{11})^{2-}$ clusters, thus the name COSAN is an acronym for CObalt SANdwich.

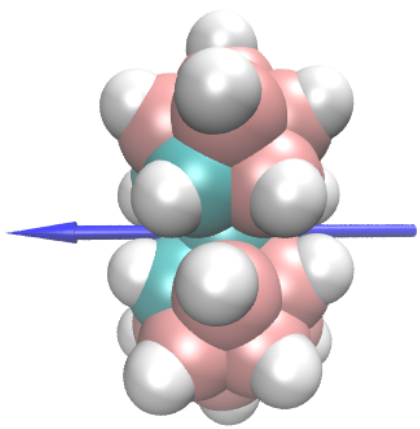

Figure 4.2: *Cisoid isomer of the negatively COSAN cluster with the corresponding electrical dipole moment drawn as a blue arrow. The Cobalt atom can be seen in the middle of the cluster sandwished by the two dicarbolide nido* $- (C_2B_9H_{11})^{2-}$ *groups*

It is interesting to model the COSAN molecule because of its shape (see Fig 4.2), the delocalized charge, and quite strong dipole moment that points out from the short side of the molecule (see Fig 2). It has been proposed that it is a Θ shaped amphiphile[31] which means that unlike a normal amphiphile that has a hydrophilic head and a hydrophobic tail, COSAN has two hydrophobic regions with a hydrophilic ring around the middle. Also like any other amphiphile, the COSAN cluster forms bigger aggregates in aqueous solutions like micelles and vesicles.[31]

We modelled the COSAN cluster by using an all atom approach which would allow us to study the explicit interaction of the COSAN cluster with the solvent, as well as the solvents effect on the pairwise interaction between two COSAN clusters. The general way of doing this type of calculation is to model each atom in the simulation as LJ beads that are connected to each other by springs. How these beads are connected to each other, how strongly they are connected by the springs and if they have a charge is generally tabulated in a so-called force field. Note that since we only knew the positions of the atoms relative too each other and their charges in the COSAN cluster, we made a simplification by modeling COSAN as a stiff molecule in Paper II.

The advantages of using the all atom approach is that we get a detailed description of the system being studied and the simulation is relatively easy to setup by just knowing the internal positions of the atoms in the molecules. These are also some of the drawbacks of the approach because

i) the description is detailed, and a tiny detail somewhere in that description can have a large effect.

ii) the number of atoms that are calculated can easily reach a million, which is a number that is barely manageable by todays computers

This second point can be dealt with by for example calculating an *effective* potential. In our case we calculated the potential of mean force which is an angle averaged potential which could possibly be used to calculate the aggregation of COSAN.

4.3 Patchy Particles

A model that lies between the off-centered dipole model and the all atom model in terms of detail is the Patchy Particle model (PPM). As the name

implies the particles are modeled as a series of connected patches each of which can have a specific characteristic such as for example hydrophobic or hydrophillic patches. A specific type of patchy particles are Charged Patchy Particles (CPP)[32] used in Paper III and an example of which can be seen in Figure 4.3. As the name suggests, the CPP is a charged particle that has negative and positive patches. In our case we modeled the particle as a soft-sphere using the WCA-potential (see section 3.3) with explicit charges coating the surface. The overall goal of this model is to

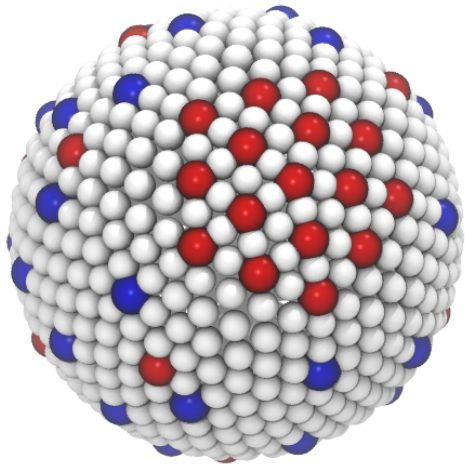

Figure 4.3: *Example of a patchy particle the blue and red beads are either negatively or positively charged while the white beads are neutral. Also one can see a distinct red patch forming on the surface of the particle. In Paper III the grey beads were replaced by a single big WCA sphere to reduce the computational cost.*

provide a more detailed way of describing proteins and colloidal particles and at the same time having a lesser computational cost than a fully atomic model. Another benefit of this model is the flexibility it provides in tuning the interactions that particles can interact with. In for exmaple our study we focus solely on electrostatic interactions between particles, while still having a more detailed charge distribution.

This leads us to how the CPP model was utilized in the scope of this work. Since 2010 there has been significant strides when it comes to the effects that multivalent electrolytes have on the phase behavior of proteins. It was noted that trivalent salts such as YCl_3 has an enhancing effect on the crystallization of proteins.[33] The follow up studies of this phenomenon saw that some proteins such as Human Serum Albumin would attract, dissolve and attract again as the salt concentration increased-

cite.[34,35,36,37,38,39,40,41,42] Thus the CPP model seemed a good choice to study the underlying electrostatic interactions of this phenomenon.

4.4 Reduced units

A helpful tool to use when designing a model or performing simulations are the reduced units. By choosing some convenient basic units we express all other quantities in terms of those basic units.[15] If we take the Lennard-Jones potential as an example (eq. 16) it is a good idea to express the unit of length in terms of σ and units of energy in terms of ϵ.

$$r^* \equiv r/\sigma \tag{4.3}$$

$$u^* \equiv u/\epsilon \tag{4.4}$$

This will give us an expression for LJ potential that looks the following.

$$u^*(r^*) = 4\left[\left(\frac{1}{r^*}\right)^{12} - \left(\frac{1}{r^*}\right)^{6}\right] \tag{4.5}$$

This will also give us for example reduced temperature as $T^* = kT\epsilon^{-1}$ and reduced density as $\rho^* = \rho\sigma^3$. The main reason for using reduced units is that many combinations of ϵ, σ, T and ρ correspond to the same state in reduced units. Thus allowing us to see significance of simulations that we otherwise would have overlooked. Also, by using reduced units we can model poperties without having to actually implement them. As an example magnetic dipoles can be modeled as electric dipoles with reduced units. There is also a practical advantage in that all quantities of interest are of order 1. This will eliminate problems with floating numbers overflow from a programming aspect and will enable you to more easily detect errors and bugs during your calculations.

Chapter 5

Summary of the Results

Overall this project focused on studying anisotropic interactions and how they affect the self-assembly of both small and large particles. Here is a short summary of the results.

5.1 Paper I

In Paper I we studied the self-assembly of colloidal particles as described experimentally by S.Saccana et al. By means of Monte Carlo simulations and through the use of the off-centered dipole model (see section 4.1) we were able to reproduce the observed self-assembly. These simulations became an indicator to what the model can achieve as well as giving some estimate of the strength of the dipole moment that is needed for this self-assembly to work.

5.2 Paper II

In Paper II we focus on the COSAN cluster (see section 4.2). By utilizing a rigid all atom model of the cluster in explicit water by means of Molecular dynamics simulations. We studied the solvation and the COSAN-COSAN interaction free energy via the potential of mean force (PMF). The resulting PMF as well as the solvation of the cluster indicate to an attraction dominated by hydrophobic interactions with the surrounding solvent. Because of this the electrostatics display a counter intuitive behavior at sort range with anion-anion attraction and anion-cation repulsion that may affect assembly at longer length scales.

5.3 Paper III

In this paper we focused on the Charged Patchy Particle Model and the effect that monovalent and trivalent ions have on the interactions between particles. We found that even milli-molar concentrations of salt will have a significant effect on the orientational space of the system and thereby perturb directional interactions. We also found that the valency of the electrolyte has a strong effect on the attraction or repulsion between two CPPM particles.

5.4 Paper IV

We focused on expanding the existing Wolf-method (see section 3.4) to account for long-ranged dipolar interactions. The method's efficiency and accuracy was compared to well established techniques such as the Ewald summation and Reaction field for Stockmayer fluids. We also did a scan of parameters to know when the method is valid, giving some rules of thumb to which parameters to use.

Chapter 6

Conclusions and Outlook

This project has been about studying anisotropic particles using computer simulations. The main advantage of a computational approach to study these types of particles is the ability to freely alter parameters that experimentally would be difficult or impossible. Also, the advantage of computer simulations is the potential to get insight on how a system looks like on the microscopic level.

In the case of the first paper, a model was designed from basic pair potentials for a specific purpose, namely to study the self-assembly of magnetic particles with an off-centered dipole moment. On the other hand the approach for Paper II was somewhat different. We used an all-atom approach to get insight on the *interaction mechanism* between the particles, thus enabling us to design an effective pair potential that will fit these particles specifically. The model used in Paper III falls in between the models of Paper I and II in terms of the details that are present in the model as we attempt to describe a globular protein as a soft repulsive sphere with electrostatic patches in an attempt to study its behavior in the presence of trivalent salt. Finally in paper IV we expanded on the Wolf-method to calculate electrostatic dipole interactions and studied the parameter space where the method could be implemented.

The ability to change the details of a model is a powerful tool to conceptualize the important properties of the real system. Tailoring a model to a specific system is thus a way of speeding up calculations without losing the overall behavior of the system.

With new challenges that science as a whole faces; be they politically, academically or industrially motivated. It is clear that the ability to predict

properties and behavior of materials using “financially cheap” computer simulations and theoretical models, instead of spending lots of money and resources on experimental setups, is going to be something that people will naturally be drawn to do. As more of the predictions made by computer simulations lead to experimentalists successfully developing new materials. Designing new more accurate models that utilize the full power of the emerging computational technology or better coarse grained models, that can run on a toaster if need be, will become more and more important.

Lastly the vast availability of standard computation packages is very useful for science at large, but this can also be a curse since it is easy to fall into the trap of using these packages as a black box without understanding the underlying theory. It is however only once you get into designing models yourself that you realize the full potential of simulations as well as their drawbacks.

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