A Microscopic Approach to Van-der-Waals Interactions between Nanoclusters: the Coupled Dipole Method

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Abstract

The Coupled Dipole Method (CDM) for the calculation of the interaction energy between nanoclusters is introduced. This method is then used to calculate the static polarizability of nanoclusters. We investigate the interaction energy between 2 nanoclusters and extend the method to investigate the influence of an external electric field. Furthermore we examine if clusters prefer a linear alignment over compact clustering. We further extend the method to incorporate nanoclusters built up from different kinds of particles. We use this to investigate capped particles. Finally we look at different ways of introducing an intervening solvent.
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## Contents

1 History ........................................ 7
   1.1 History of Van-der-Waals forces ............... 7
   1.2 Van-der-Waals interaction according to London 8

2 Theory ....................................... 10
   2.1 Static Polarizability ........................ 10
   2.2 Interaction between two clusters ............ 12
   2.3 Interactions in an external electric field .... 15
   2.4 Interactions between clusters consisting of different species of particles 16
   2.5 Polarization Catastrophe ..................... 17
   2.6 Discussion ................................ 19

3 Static Polarizability of clusters in an external electric field ........... 20
   3.1 Static polarizability of a finite cube ......... 20
   3.2 Static polarizability of a finite sphere ....... 21
   3.3 Static polarizability of an infinite cube or sphere 22
   3.4 Approximations ................................ 23
      3.4.1 Approximation 1: Dividing a cube into smaller cubes 23
      3.4.2 Approximation 2: Hollow Cubes and Spheres .... 24
   3.5 Local enhancement factors ..................... 25
   3.6 Exploiting Symmetry .......................... 27
   3.7 Enhancement factors of linear clusters ......... 29
   3.8 Static polarizability not parallel to applied field 30
   3.9 Discussion ................................ 31

4 VdW interactions between two clusters in vacuum ....................... 33
   4.1 Reproduction of literature results for dimers and decamers .... 33
   4.2 Influence of external electric field on interactions .......... 34
   4.3 Comparison to pairwise sum method ............. 36
   4.4 Chain formation ................................ 38
      4.4.1 Atoms .................................... 38
      4.4.2 Cubic Clusters ............................ 40
   4.5 Interaction as function of particle number ............ 41
   4.6 Discussion ................................ 42

5 Interactions between capped spheres ................................ 46
   5.1 Steric Interactions ............................ 46
   5.2 Description of Model .......................... 47
   5.3 Discussion of parameters ...................... 48
   5.4 Discussion ................................ 50
6 Interactions in solvent

6.1 First attempt to introduce a solvent: CDMS-1
   6.1.1 Motivation ................................................................. 51
   6.1.2 Results ................................................................. 51

6.2 Refining the method: CDMS-2 ........................................... 53
   6.2.1 Motivation ................................................................. 53
   6.2.2 Results ................................................................. 54

6.3 Following the pairwise sum method: CDMS-3 ......................... 54

6.4 Treating the solvent as fluctuating dipoles: CDMS ................... 56
   6.4.1 Description of model .................................................... 56
   6.4.2 Results ................................................................. 56
   6.4.3 Comparison to approximations CDMS-1-3 ......................... 58

6.5 Including the permanent dipoles ........................................... 58

6.6 Discussion ........................................................................... 59

7 Conclusion ............................................................................. 61
Foreword

In this document I will present the results of my research for my master thesis in theoretical physics at the University of Utrecht. I performed this research under supervision of René van Roij and I collaborated closely with Bas Kwaadgras and Marjolein Dijkstra. The subject of my thesis was the Coupled Dipole Method (CDM) and its applications. This method is a microscopic approach to the Van-der-Waals interaction between nanoclusters. I will start by giving some background information on Van-der-Waals forces. In chapter 2 I will introduce the theory behind the Coupled Dipole Method. The following chapters will deal with my results. In chapter 3 I will present my results concerning the static polarizability of a single nanocluster. Here I will focus mainly on the static polarizability of cubic an spherical clusters and I will investigate its dependence on the cluster size. Furthermore I will investigate the limit for infinite size clusters. In chapter 4 I will give some results for the interaction between 2 nanocluster consisting of a single atomic species. Here I will also investigate chain formation between these clusters and I will investigate the effect of an external electric field on this interaction. Furthermore I will compare the results with the pairwise sum method. The next part, chapter 5, will deal with interactions between spherical cluster which have a capping layer to prevent aggregation. Finally in chapter 6 I will investigate different methods of introducing a solvent into our system. I will end every chapter with a discussion where I will outline how my results compare to those known from the literature.
Chapter 1

History

1.1 History of Van-der-Waals forces

Van-der-Waals (VdW) forces have been studied ever since Johannes van der Waals suggested them in his equation of state in his thesis, which appeared in 1873 and for which he would receive the Nobel Prize in 1910. These forces describe the attraction between molecules that are now known to originate from the quantum-mechanical fluctuations of the electrons. It is well known that they play a big role in coalescence, crystallization and the formation of instabilities. In recent years a lot of progress has been made in the measurement of VdW-related properties including the interaction between solid bodies, the thickness of helium films, the frequency and phase shifts of atoms in cavities as well as the ability to disperse nanoclusters in suspensions [1]. In this thesis I will investigate the Van-der-Waals forces between nanoclusters, which is important because this affects self-assembly of the nanoclusters. Therefore it is important to have a good theoretical understanding of the theory behind these interactions. London [2] showed that the potential $V(r)$ of the VdW interaction of two neutral, interacting point particles is given by

$$V(r) = -\frac{C}{r^6}, \quad (1.1)$$

where $r$ is the distance between the particles and $C$ is a constant depending on the type particles and the medium in which the particles reside. In the next section I will show how he obtained this result. However when there are more particles in play, the situation becomes much more complicated. The simplest way, and the most used in the literature, is the pairwise sum method, which gives the interaction between a cluster A consisting of $N_A$ particles and a cluster B consisting of $N_B$ particles as the sum over all two-body interactions between a particle $i$ in cluster A and a particle $j$ in cluster B. The potential energy of the interaction is then given by

$$V = \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} V_{ij}(r_{ij}) = -\sum_{i=1}^{N_A} \sum_{j=1}^{N_B} \frac{C_{ij}}{r_{ij}^6}. \quad (1.2)$$

However this pairwise approximation abolishes all many body effects, which is expected to be inaccurate in dense systems. A second method of calculating the VdW interactions is the so called Dzyaloshinskii-Lifshitz-Pitaevskii theory (DLP) which is based on quantum-electrodynamic fluctuations as described by macroscopic frequency dependent dielectric properties. This DLP method therefore assumes that we have a sufficiently large separation and sufficiently large bodies such that a bulk continuum description of the dielectric response is warranted. However this means it does not work well for the nanoclusters considered in this thesis [1] and will therefore not be discussed any further. Instead I will use a microscopic approach called the Coupled Dipole Method or CDM for short, which is known to be equivalent to DLP in the macroscopic limit. In the next chapter I will explain how this method works.
1.2 Van-der-Waals interaction according to London

Here I will show how London [2] obtained the form for the VdW interaction given in equation 1.1. This method can be found in many books on quantum mechanics and I will use the book by Bransden and Joachain [3] as my source. For simplicity I will discuss only the case where both point particles are hydrogen atoms, so both consist of a single proton and a single electron. The first proton is situated at A and the second one at B, whereas the first electron is located at position 1 and the second at position 2. The distance AB I call $R$ and this is taken as the x-axis. Furthermore the distance between A and the first electron I call $r_{1A}$ and in similar fashion I define $r_{1B}$, $r_{2A}$ and $r_{2B}$. The distance between the two electrons I label $r_{12}$. The setup of the system is also given in figure 1.1. We now fix the internuclear distance $R$ and then consider

\[
H = H_A + H_B + V(1,2),
\]

(1.3)

where $H_A$ is the Hamiltonian of atom A (both proton and electron), $H_B$ for atom B and $V(1,2)$ is the interaction energy between the two atoms. The three components are given by [3]:

\[
H_A = -\frac{\hbar^2}{2m} \nabla^2 r_{1A} - \left(\frac{e^2}{4\pi\epsilon_0}\right) \frac{1}{r_{1A}},
\]

(1.4)

\[
H_B = -\frac{\hbar^2}{2m} \nabla^2 r_{2B} - \left(\frac{e^2}{4\pi\epsilon_0}\right) \frac{1}{r_{2B}},
\]

(1.5)

\[
V(1,2) = \left(\frac{e^2}{4\pi\epsilon_0}\right) \left(\frac{1}{R} + \frac{1}{r_{12}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}}\right),
\]

(1.6)

where $\hbar$ is the Planck constant, $m$ is the electron mass, $e$ is the elementary charge and $\epsilon_0$ the vacuum permittivity. We remark that the interaction potential $V(1,2)$ is just a simple Coulomb interaction potential. Because we are interested in the Van-der-Waals forces we can assume $R$ to be much larger than the atomic distances $r_{1A}$ and $r_{2B}$, and as a result we can treat $V(1,2)$ as a perturbation. We now define the Cartesian coordinates of point 1 w.r.t. point A as origin to be $x_1$, $y_1$ and $z_1$ and similarly those of point 2 w.r.t. point B as origin as $x_2$, $y_2$ and $z_2$. Then we find that

\[
r_{12} = \left[ (x_2 - x_1 + R)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2 \right]^{1/2},
\]

(1.7)

\[
r_{1B} = \left[ (x_1 - R)^2 + y_1^2 + (z_1)^2 \right]^{1/2},
\]

(1.8)

\[
r_{2A} = \left[ (x_2 + R)^2 + y_2^2 + (z_2)^2 \right]^{1/2}.
\]

(1.9)
We can now expand all the terms in equation 1.6 in Taylor series in powers of $1/R$ and we obtain

$$\frac{1}{r_{12}} = \frac{1}{R} \left[ 1 - \frac{x_2 - x_1}{R} - \frac{2(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2}{2R^2} + \cdots \right],$$  \hspace{1cm} (1.10)

$$\frac{1}{r_{1B}} = \frac{1}{R} \left[ 1 + \frac{x_1}{R} - \frac{2x_1^2 + y_1^2 + z_1^2}{2R^2} + \cdots \right],$$  \hspace{1cm} (1.11)

$$\frac{1}{r_{2A}} = \frac{1}{R} \left[ 1 - \frac{x_2}{R} - \frac{2x_2^2 + y_2^2 + z_2^2}{2R^2} + \cdots \right].$$  \hspace{1cm} (1.12)

If we combine equations 1.10-1.12 with equation 1.6 we see that the terms in $1/R$ and $1/R^2$ cancel, so that for large $R$ we obtain

$$V(1, 2) = \left( \frac{e^2}{4\pi\varepsilon_0} \right) \frac{1}{R^3} (-2x_1x_2 + y_1y_2 + z_1z_2).$$  \hspace{1cm} (1.13)

Now we are ready to perform the perturbation theory. We call the energy of the unperturbed system in which both hydrogen atoms are in the ground state $2E_0$ and the unperturbed wave function is $\psi_0(r_1A)\psi_0(r_2B)$, which satisfies the equation

$$(H_A + H_B - 2E_0)\psi_0(r_1A)\psi_0(r_2B) = 0.$$  \hspace{1cm} (1.14)

We can now write the total energy of the system by

$$E = 2E_0 + E^{(1)} + E^{(2)} + \cdots,$$  \hspace{1cm} (1.15)

where $E^{(n)}$ is calculated from the $n$th-order perturbation theory. We find that the first-order correction term

$$E^{(1)} = \int \psi^*(r_1A)\psi^*(r_2B)V(1, 2)\psi(r_1A)\psi(r_2B)dr_{1A}dr_{2B}$$  \hspace{1cm} (1.16)

vanishes because the matrix elements of angular dependent terms like $x_1$ are zero when taken between spherical symmetric wave functions. The next term however does not vanish and is given by

$$E^{(2)} = \sum_{j\neq 0} \frac{\langle \psi'_0 | V | \psi'_j \rangle \langle \psi'_j | V | \psi'_0 \rangle}{E_0 - E_j},$$  \hspace{1cm} (1.17)

where $\psi'_j = \psi_0(r_1A)\psi_0(r_2B)$, the $\psi'_j$ denote the intermediate states and $E_j$ denotes the energy in the intermediate states. We see that the numerator is always positive and behaves like $1/R^6$, whereas the denominator is always negative, since $E_j - E_0 > 0$. Therefore the interaction energy between two hydrogen atoms is approximated by

$$E^{(2)}(R) = -\frac{C}{R^6},$$  \hspace{1cm} (1.18)

where $C$ is a positive constant. We see that we have now arrived at the form given in equation 1.1.
Chapter 2

Theory

The Coupled Dipole Method (CDM) for the calculation of the Van-der-Waals (VdW) interaction was first introduced by Renne and Nijboer in a series of articles ([4], [5] and [6]). However they lacked the computing power to perform calculations for finite sized nanoclusters. More recently interest in the method has been revived by Kim, Sofo, Velegol and Cole ([1], [7] and [8]), who used CDM to calculate both static polarizabilities of a single nanocluster and the interactions between 2 nanoclusters. In this chapter I will present the theory behind the CDM as outlined by Kim et al. I will start with discussing the theory for calculating the static polarizability in section 2.1. Next I will discuss the theory of interactions between nanocluster as described by both Kim et al. and Renne and Nijboer. This will be done in section 2.2. Then I will present two extensions of this theory. First of all in section 2.3 I will show how we can incorporate an external electric field into the CDM. Finally in section 2.4 I will show how the model changes when we have clusters consisting of different species of particles before discussing the limitations of the model due to the polarization catastrophe in section 2.5.

2.1 Static Polarizability

Here I will show how to calculate the static polarizability of a finite cluster. I will follow the article by Kim et al. [7]. The basic principle of the CDM is to view every particle as a fluctuating dipole; the VdW interaction is then a result of the interaction between these fluctuating dipoles. For simplicity we use the Lorentz model, in which an atom is viewed as a nucleus and an electron bound to it by an isotropic harmonic force characterized by a spring-constant $m\omega_0^2$ with $m$ the electron mass and $\omega_0$ the eigenfrequency of the harmonic potential. When an electric field $E_0$ is applied, the electron will be displaced with respect to the nucleus and as a result the atom will get a polarization equal to

$$p = \alpha_0 E_0,$$

where the atomic polarizability $\alpha_0$ is given by

$$\alpha_0 = \frac{e^2}{\epsilon_0 m \omega_0^2},$$

where $e$ is the elementary charge and $\epsilon_0$ is the vacuum permittivity. We note that in the SI unit system, which I will use throughout this thesis, $\alpha_0$ has the dimension of volume. If we place the dipole in the origin, then at position $r$ it creates an electric field equal to

$$E(r) = T(r) \cdot p,$$

with

$$T(r) = \frac{(3\mathbf{r}\hat{r} - \mathbf{I})}{r^3},$$
where $I$ denotes the $3 \times 3$ identity matrix and $\hat{r} = r/|r|$. We now consider the case of a cluster of $N$ particles in the external electric field $E_0$. Every particle is an isotropic oscillator and we denote the equilibrium position of the $j$th particle by $r_j$. We see that the local electric field at position $r_j$ is given by

$$E(r_j) = E_{j}^{loc} = E_0 + E_{j}^{int},$$

(2.5)

where $E_{j}^{int}$ is the field created by the induced dipoles of neighboring particles. From elementary electrostatics it follows that

$$E_{j}^{int} = \sum_{i=1, i \neq j}^{N} T(r_{ij}) \cdot p_i = \sum_{i=1, i \neq j}^{N} T_{ji} \cdot p_i.$$  

(2.6)

Now we can define the induced dipole moment of the cluster $p_c$ as

$$p_c = \sum_{j=1}^{N} p_j,$$  

(2.7)

and the polarizability tensor of the cluster ($\alpha_c$) as

$$p_c = \alpha_c \cdot E_0.$$  

(2.8)

Furthermore we know that the induced dipole moment of the $j$th particle is given by

$$p_j = \alpha_0 \cdot E_{j}^{loc},$$  

(2.9)

with $\alpha_0$ the known atomic polarizability of the particle. It is important here to note that the atomic polarizability is a scalar whereas the static polarizability of the cluster is a tensor.

For simplicity we now introduce $E_0 = E_0 e$ and $p'_j = p_j/(\alpha_0 E_0)$. By combining equations 2.5-2.9, we obtain $3N$ coupled linear equations

$$p'_j - \alpha_0 \sum_{i=1, i \neq j}^{N} T_{ji} \cdot p'_i = e.$$  

(2.10)

Let $\mathcal{P}$, $\mathcal{E}$ and $\mathcal{T}$ be $3N$ vectors and a $3N \times 3N$ matrix build up from the individual $p'_j$, $e$ and $T_{ji}$ respectively in the following manner:

$$\mathcal{P} = \begin{pmatrix} p'_1 \\ \vdots \\ p'_N \end{pmatrix}, \quad \mathcal{E} = \begin{pmatrix} e \\ \vdots \\ e \end{pmatrix},$$

$$\mathcal{T} = \begin{pmatrix} 0 & T_{12} & \cdots & T_{1N} \\ T_{21} & \ddots & \vdots \\ \vdots & \ddots & \ddots \\ T_{N1} & \cdots & T_{(N-1)N} & 0 \end{pmatrix}.$$  

(2.11)

(2.12)

Then we can rewrite equation 2.10 as

$$\mathcal{P} = (1 - \alpha_0 \mathcal{T})^{-1} \cdot \mathcal{E}.$$  

(2.13)

We see that this equation is easy to solve numerically by matrix inversion. Moreover if we have the solution we can find the polarization of the cluster using equation 2.7. Next we need to find the polarizability tensor
as defined by equation 2.8. We can find the first column by fixing the electric field in the $x$-direction and then we find that

$$\alpha_{\text{cluster}}^{(1,1)} = \alpha_0 \sum_{j=0}^{N-1} P_{3j+i}. \quad (2.14)$$

The other 6 entries can be found by taking the electric field in the $y$- and $z$-direction respectively. Note however that as most of the clusters I will study will have a large degree of symmetry, this will not always be necessary. First of all, it can be shown that the polarizability tensor is always symmetric as long as the cluster consists of only one species of particles. Secondly we see that if a cluster is symmetric under interchanging the $x$, $y$, and $z$-axes then from symmetry the polarizability in the $y$- and $z$-directions has to be the same as in the $x$-direction. Furthermore we see that if the cluster is symmetric under mirroring in one of the axis then the polarizability in that direction has to be a diagonal, i.e. then we cannot have a field in the $x$-direction creating a polarizability in the $y$-direction. If we have a cluster that satisfies both these symmetry conditions (like a cube or a sphere), the polarizability tensor will become a multiple of the identity matrix and we can uniquely define it by the value of this multiple. Therefore in this case, following the article by Kim et al., we can uniquely define the enhancement factor $f$ by

$$f = \frac{\alpha_{\text{cluster}}^{(1,1)}}{N\alpha_0} = \frac{1}{N} \sum_{j=0}^{N-1} P_{3j+1}. \quad (2.15)$$

However if one of these symmetry conditions is not satisfied (for instance when dealing with a linear cluster), we cannot define an enhancement factor, but only an enhancement tensor $f$. In most of the interesting cases the second symmetry condition will however hold in all directions, which means that our enhancement tensor will be diagonal. Furthermore, for a linear cluster along the $x$-axis we can also interchange the $y$- and $z$-directions and see that therefore the enhancement tensor can be uniquely defined by two values. Following the article by Kim et al. [7] I call these the enhancement factor parallel and orthogonal to the applied electric field. I will only briefly discuss clusters whose enhancement tensor has non-zero entries outside of the diagonal and in this case I will give the full form of the tensor.

### 2.2 Interaction between two clusters

Now I will show how we can use the CDM to calculate the interaction energy between two nanoclusters. In this section I will do the calculation in absence of an external electric field and assume that the clusters exist of just one species of particles. In the next section I will show what the influence of an external electric field is, and in section 2.4 I will show how we can extend the method to include multiple types of particles. The system we consider now consists of $2N$ isotropic oscillators ($N$ in every cluster) with fixed equilibrium positions $r_1, \ldots, r_{2N}$. We call the deviation of the $i$th oscillator from its equilibrium position $u_i$. The Hamiltonian of this system is given by

$$H = \sum_{i=1}^{2N} \frac{p_i^2}{2m} + \frac{m\omega_0^2}{2} \sum_{i=1}^{2N} u_i^2 - \frac{e^2}{2\epsilon_0} \sum_{i,j=1}^{2N} u_i \cdot T_{ij} \cdot u_j, \quad (2.16)$$

where $p_i$ denotes the linear momentum of the $i$th particle and the other symbols are as defined above. In order to reduce the number of sums in the equations we again introduce the vectors $\mathcal{U}$, $\mathcal{P}$ and the matrix $\mathcal{T}$ which are built up from the $u_i$, $p_i$ and the $T_{ij}$ respectively. Then we can rewrite the Hamiltonian from equation 2.16 in the form

$$H = \frac{p^2}{2m} + \frac{m\omega_0^2}{2} \mathcal{U}^2 - \frac{e^2}{2\epsilon_0} \mathcal{U}^T \mathcal{T} \mathcal{U} \quad (2.17)$$

$$= \frac{p^2}{2m} + \mathcal{U}^T \mathcal{\Omega} \mathcal{U}, \quad (2.18)$$
where

$$\Omega = \frac{m\omega_0^2}{2} \left( I - \alpha_0 T \right) = \frac{m\omega_0^2}{2} \left( \begin{array}{cc} I - \alpha_0 T_1 & -\alpha_0 T_2 \\ -\alpha_0 T_2 & I - \alpha_0 T_1 \end{array} \right)$$

(2.19)

with $T_1$ an $N \times N$ matrix denoting the intra cluster and $T_2$ an $N \times N$ matrix denoting the inter cluster interactions. The Hamiltonian equations of motion

$$\frac{\partial H}{\partial U} = -\dot{P} \quad \text{and} \quad \frac{\partial H}{\partial P} = \dot{U}$$

(2.20)

yield

$$m\ddot{U} = -2\Omega U,$$

(2.21)

where the dot denotes the time derivative. Making the Ansatz that $U(t) = U(0)e^{i\omega t}$, we find the eigenvalue equation

$$m\omega^2 U = 2\Omega U,$$

(2.22)

such that the eigenfrequencies $\omega_k$ are related to the eigenvalues $\lambda_k$ of $\Omega$ by

$$\omega_k = \sqrt{2\lambda_k/m}$$

(2.23)

for $k = 1, 2, \ldots, 6N$. Furthermore if $\lambda_k$ is an eigenvalue of $T$ we see from equation 2.19 that

$$\lambda_k = m\omega_0^2 (1 - \alpha_0 \lambda_k),$$

(2.24)

and hence

$$\omega_k = \omega_0 \sqrt{1 - \alpha_0 \lambda_k}.$$  

(2.25)

Assuming the oscillator-system to be in the quantum-mechanical ground state, which is a good approximation for ambient temperatures and typical atomic parameters, we can write the total energy of the cluster as [4]:

$$V_{tot} = \frac{\hbar^2}{2} \sum_{k=1}^{6N} \omega_k,$$

(2.26)

where $\hbar$ denotes Planck’s constant. However as we are only interested in the VdW interaction energy we have to subtract the potential energy stored in 2 clusters at an infinite distance from each other. As we assumed the clusters to be equal we can do the calculation for one and then multiply the answer by 2. We start by introducing the $3N$ vectors $U'$ and $P'$ and the $3N \times 3N$ matrix $T'$ in a similar way as before but now for the case of only 1 cluster. We then get the Hamiltonian

$$H' = \frac{p'^2}{2m} + \frac{m\omega_0^2}{2} U'^T (I - \alpha_0 T') U'.$$

(2.27)

Following the procedure above we find eigenvalue equation

$$m\omega^2 U' = m\omega_0^2 \Omega U'.$$

(2.28)

If we denote the eigenvalues of $T'$ by $\lambda_k'$ we see that if

$$\omega_k' = \omega_0 \sqrt{1 - \alpha_0 \lambda_k'}$$

(2.29)
it satisfies equation 2.28. Therefore we find for the potential energy of 1 cluster

\[ V'_\text{tot} = \frac{\hbar}{2} \sum_{k=1}^{3N} \omega'_k. \]  

So if we now define

\[ \omega''_k = \begin{cases} 
\omega'_k & \text{if } k \leq 3N \\
\omega'_{k-3N} & \text{if } k > 3N 
\end{cases} \]  

we find for the interaction energy of 2 clusters

\[ V'_{\text{int}} = \frac{\hbar}{2} \sum_{k=1}^{6N} (\omega_k - \omega''_k). \]  

So we see that all we need to do to calculate the VdW interaction between two clusters, is to calculate the eigenvalues of a $2N \times 2N$ matrix and of a $N \times N$ matrix. The theory described so far follows the work by Renne and Nijboer ([4], [5] and [6]) and by Kim et al. ([1] and [8]). Here I will show how the CDM reduces to equation 1.1 when $N = 1$. So we have two clusters both consisting of a single particle and we choose our coordinates such that the separation between them is given by $r = (r, 0, 0)^T$. From equation 2.6 we see that the matrix $T$ is then given by

\[ T = \begin{pmatrix}
0 & 0 & 0 & \frac{2}{r^3} & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{-1}{r^3} & 0 \\
\frac{2}{r^3} & 0 & 0 & 0 & 0 & \frac{-1}{r^3} \\
0 & \frac{-1}{r^3} & 0 & 0 & 0 & 0 \\
0 & 0 & \frac{-1}{r^3} & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{-1}{r^3} & 0 & 0
\end{pmatrix}. \]  

It is now an easy calculation to find that the eigenvalues of this matrix are given by

\[ \lambda_1 = \frac{-2}{r^3}, \quad \lambda_2 = \frac{-1}{r^3}, \quad \lambda_3 = \frac{-1}{r^3}, \]  

\[ \lambda_4 = \frac{1}{r^3}, \quad \lambda_5 = \frac{1}{r^3}, \quad \lambda_6 = \frac{2}{r^3}. \]  

Furthermore for large separations we see that we can expand equation 2.25 in the form

\[ \omega_k \approx \omega_0 \left(1 - \frac{\alpha_0 \lambda_k}{2} - \frac{\alpha_0^2 \lambda_k^2}{8}\right). \]  

We note that, when we now sum all the $\omega_k$, the second term in this equation cancels due to symmetry in the eigenvalues. Furthermore a third order correction term would cancel due to the same reason and as we will see later on that we restrict ourselves to the case $\alpha_0 / r^3 < 0.2$ we see that fourth order terms and higher can be neglected easily. So we find from equation 2.26 that the total energy of the system equals

\[ V_{\text{tot}} = \frac{\hbar \omega_0}{2} \left(6 - \frac{3 \alpha_0^2}{2r^6}\right), \]  

and as $T' = 0$ we see that $V'_{\text{tot}} = \frac{3\hbar \omega_0}{2}$. So we find that the VdW interaction potential is given by

\[ V_{\text{int}}(r) = -\frac{3\hbar \omega_0 \alpha_0^2}{4r^6}, \]  

which coincides with equation 1.1 if $C$ satisfies

\[ C = \frac{3\hbar \omega_0 \alpha_0^2}{4}. \]  

So we found that for single particles the CDM result agrees with the result by London as discussed in chapter 1.
2.3 Interactions in an external electric field

Here I will extend the theory to encompass the effects of a homogeneous external electric field $E_0$. The introduction of the electric field causes the Hamiltonian to change into

$$H = \sum_{i=1}^{2N} \frac{p_i^2}{2m} + \frac{m\omega_0^2}{2} \sum_{i=1}^{2N} u_i^2 - \frac{e^2}{2\epsilon_0} \sum_{i,j=1}^{2N} u_i \cdot T_{ij} \cdot u_j - e \sum_{i=1}^{2N} u_i \cdot E_0. \quad (2.40)$$

Following the procedure above we rewrite this into

$$H = \frac{p^2}{2m} + \frac{m\omega_0^2}{2} \mathcal{U}^2 - \frac{e^2}{2\epsilon_0} \mathcal{U}^T \mathcal{U} - e \mathcal{U}^T \mathcal{E} \quad (2.41)$$

$$= \frac{p^2}{2m} + \mathcal{U}^T \mathcal{\Omega} \mathcal{U} - e \mathcal{U}^T \mathcal{E}, \quad (2.42)$$

where $\mathcal{E}$ is the vector built up from $2N$ copies of $E_0$. If we now introduce $\mathcal{A}$ such that

$$\mathcal{A} = \frac{e}{2} \mathcal{\Omega}^{-1} \mathcal{E}, \quad (2.43)$$

we can rewrite equation 2.40 in the form

$$H = \frac{p^2}{2m} + (\mathcal{U} - \mathcal{A})^T \mathcal{\Omega}(\mathcal{U} - \mathcal{A}) - \frac{e^2}{4} \mathcal{E}^T \mathcal{\Omega}^{-1} \mathcal{E}. \quad (2.44)$$

Now it is easy to see that the equations of motion change into

$$m \frac{\partial^2}{\partial t^2} (\mathcal{U} - \mathcal{A}) = -2\mathcal{\Omega}(\mathcal{U} - \mathcal{A}). \quad (2.45)$$

If we now change the Ansatz into $(\mathcal{U} - \mathcal{A})(t) = (\mathcal{U} - \mathcal{A})(0)e^{i\omega t}$ we find the eigenvalue equation

$$m\omega^2(\mathcal{U} - \mathcal{A}) = 2\mathcal{\Omega}(\mathcal{U} - \mathcal{A}). \quad (2.46)$$

If we now assume that the eigenvalues of $\mathcal{T}$ are known and denoted by $\lambda_k$, we see that the eigenfrequencies $\omega = \omega_k$ satisfy

$$\omega_k = \omega_0 \sqrt{1 - \alpha_0 \lambda_k}. \quad (2.47)$$

Hence the potential energy of the system is given by

$$V_{tot} = \hbar \sum_{k=1}^{6N} \omega_k - \frac{e^2}{4} \mathcal{E}^T \mathcal{\Omega}^{-1} \mathcal{E}. \quad (2.48)$$

We should note that the second term in this equation can also be written as $\frac{1}{2} \mathbf{p}_c \cdot \mathbf{E}_0 = \frac{1}{2} (\alpha_c \cdot \mathbf{E}_0) \cdot \mathbf{E}_0$, where $\mathbf{p}_c$ is the polarization both clusters combined as calculated in section 2.1. Therefore we see that if the static polarization of a cluster is a multiple of the identity matrix, as is the case for simple cubic and spherical clusters, the energy of the cluster in an external electric field will not depend on the direction of the field but only on the field strength. Therefore we see that an external electric field will have no influence on the orientation of a single cubic cluster. Intuitively this might seem strange as one might expect a cubic cluster to align its diagonal with the external field. However one should then note that the diagonal of a cubic cluster does not contain more dipoles than one of the edges and therefore it should not prefer this direction.

Again we have not yet obtained the interaction energy and we still need to subtract the energy contained in the 2 clusters at infinite separation, but now also taking the electric field in consideration. If we define $\mathcal{T}'$,
\( \Omega', \omega'_k \) and \( \omega''_k \) in the same way as in the previous section, we can repeat the calculation above and we find for the interaction energy of 2 clusters in the electric field

\[
V_{\text{int}} = \frac{\hbar}{2} \sum_{k=1}^{6N} (\omega_k' - \omega'_k) - \frac{e^2}{4} \left( \mathcal{E}^T \Omega^{-1} \mathcal{E} - 2\mathcal{E}'^T \Omega'^{-1} \mathcal{E}' \right). \tag{2.49}
\]

We see that we can write this in the form

\[
V_{\text{int}} = V_{\text{int}}^0 + V_{\text{int}}^E, \tag{2.50}
\]

where \( V_{\text{int}}^0 \) is the interaction in absence of the external electric field and \( V_{\text{int}}^E \) is the correction term due to the electric field. It is convenient to write the potential energy in units of \( \frac{\hbar \omega_0}{2} \) which gives

\[
2 \frac{V_{\text{int}}}{\hbar \omega_0} = \sum_{k=1}^{6N} \left( \sqrt{1 + \alpha_0 \lambda_k} - \sqrt{1 + \alpha_0 \lambda'_k} \right)
- \frac{\alpha_0 \epsilon_0}{\hbar \omega_0} \left( \mathcal{E}^T (I - \alpha_0 \mathcal{T})^{-1} \mathcal{E} - 2\mathcal{E}'^T (I - \alpha_0 \mathcal{T}')^{-1} \mathcal{E}' \right). \tag{2.51}
\]

From the second term we see that it makes sense to move to a rescaled electric field vector defined by

\[
\tilde{\mathcal{E}} = \sqrt{\frac{\alpha_0 \epsilon_0}{\hbar \omega_0}} \mathcal{E}, \tag{2.52}
\]

and a similar definition for \( \tilde{\mathcal{E}}' \). Then we find

\[
2 \frac{V_{\text{int}}}{\hbar \omega_0} = \sum_{k=1}^{6N} \left( \sqrt{1 + \alpha_0 \lambda_k} - \sqrt{1 + \alpha_0 \lambda'_k} \right)
- \left( \tilde{\mathcal{E}}^T (I - \alpha_0 \mathcal{T})^{-1} \tilde{\mathcal{E}} - 2\tilde{\mathcal{E}}'^T (I - \alpha_0 \mathcal{T}')^{-1} \tilde{\mathcal{E}}' \right). \tag{2.53}
\]

So we see that the introduction of an external electric field can be easily adapted into the theory. However we now need to calculate both the eigenvalues and the inverse of the matrices \( \mathcal{T} \) and \( \mathcal{T}' \) and this will slow down the calculation considerably. In section 4.2 I will calculate the effects of the external field on the interactions between linear clusters.

### 2.4 Interactions between clusters consisting of different species of particles

Here I will show how we can extend the theory to include different types of particles. This is needed if we want to extend our method to capped particles or if we want to include a solvent in our system. Therefore we now consider a system of \( M \) different kinds of particles. We assume that particle type \( i \) is uniquely specified by its atomic polarizability \( \alpha_0^{(i)} \) and characteristic frequency \( \omega_0^{(i)} \). The Hamiltonian can still be cast in the form

\[
H = \frac{\mathcal{P}}{2m} + \mathcal{U}^T \Omega \mathcal{U}, \tag{2.54}
\]

with a modified \( \Omega \). It is now built up from \( 3 \times 3 \) matrices \( \Omega_{ij} \) which are given by

\[
\Omega_{ij} = \frac{1}{2m} \left( \omega_0^{(i)} \right)^2 \left( \delta_{ij} \mathcal{I} - \alpha_0^{(i)} (1 - \delta_{ij}) \mathcal{T}_{ij} \right), \tag{2.55}
\]

with \( \mathcal{T}_{ij} \) as defined in equation 2.6. We can now derive the equations of motion again and they result in

\[
\ddot{\mathcal{U}} = -\mathcal{A} \mathcal{U}, \tag{2.56}
\]
where I introduced the matrix $\mathcal{A}$ which is build up from blocks
\[
A_{ij} = \frac{\Omega_{ij}}{m} = \frac{1}{2} \left( \omega_0^{(i)} \right)^2 \left( \delta_{ij} I - \alpha_0^{(i)} (1 - \delta_{ij}) T_{ij} \right)
\]
for simplicity of notation. In theory all we need to do now is to calculate the eigenvalues of $\mathcal{A}$. However we note that this matrix is no longer symmetric. As the computer programme we use to calculate the eigenvalues needs the matrix to be symmetric we have to do some more algebra. We start by writing
\[
\mathcal{A} = \mathcal{D} \mathcal{M}
\]
with
\[
\mathcal{D} = \text{diag} \left\{ \left( \omega_0^{(i)} \right)^2 \alpha_0^{(i)} \right\}
\]
and $\mathcal{M}$ build up from
\[
M_{ij} = \frac{\delta_{ij}}{\alpha_0^{(i)}} I - (1 - \delta_{ij}) T_{ij}.
\]
Note that $\mathcal{D}$ is a diagonal matrix and $\mathcal{M}$ is a symmetric matrix. Now we see that if $a_i$ is an eigenvalue and $v_i$ the corresponding eigenvector of $\mathcal{A}$ we can write
\[
a_i v_i = \mathcal{A} v_i = \mathcal{D} \mathcal{M}^{1/2} \mathcal{D}^{-1/2} v_i
\]
Multiplying both sides with $\mathcal{D}^{-1/2}$ from the left we get
\[
\mathcal{A}' w_i = a_i w_i
\]
with
\[
\mathcal{A}' = \mathcal{D}^{1/2} \mathcal{M}^{1/2},
\]
\[
w_i = \mathcal{D}^{-1/2} v_i.
\]
So we see that $a_i$ is also an eigenvalue of the symmetric matrix $\mathcal{A}'$. So we can restrict the calculation to symmetric matrices. When we have calculated the eigenvalues $a_i$, we can find the total potential energy by
\[
V_{\text{tot}} = \frac{\hbar}{2} \sum_{i=1}^{6N} \sqrt{a_i}.
\]
Again we will need to repeat the calculation for infinite separation between the clusters to obtain the interaction energy between the clusters, but as this is done in exactly the same way as before I will not repeat this here.

2.5 Polarization Catastrophe

Unfortunately the CDM model in its current form does not work for all materials. It only works for materials with a relative low atomic polarizability $\alpha_0$ compared to the interparticle separation $a_0$, because otherwise a so called polarization catastrophe occurs. In this section I will explain why and when this happens. I will start by introducing the dimensionless polarizability
\[
v = \frac{\alpha_0}{\alpha_0^*}
\]
However in other parts of this thesis I will work with a different dimensionless constant, i.e. the dimensionless interparticle distance

\[ a = \frac{a_0}{\sqrt{\alpha_0}} \]  

(2.67)

We see that \( v = 1/a^3 \) and I will use both dimensionless constants throughout this thesis. However in this chapter I will only use \( v \). I will illustrate this using a system consisting of an infinite line of particles in the \( x \)-direction all separated by \( a_0 \). Here I will follow the calculation as done by Cole and Velegol in [9]. We know that the total potential energy of the interacting dipoles is given by

\[ V = \frac{m \omega_0^2}{2} \sum_{j=1}^{\infty} x_j^2 - \frac{e^2}{4\epsilon_0 a_0^3} \sum_{j=1}^{\infty} \sum_{k>j}^{\infty} \frac{3x_j x_k - \mathbf{u}_j \cdot \mathbf{u}_k}{(k-j)^3} \]  

(2.68)

where I introduced \( \mathbf{u}_j = (x_j, y_j, z_j)^T \). We can split up into

\[ V = V_x + V_y + V_z \]

where each of these three terms is associated with a different direction,

\[ V_x = \frac{m \omega_0^2}{2} \sum_{j=1}^{\infty} x_j^2 - \frac{e^2}{4\epsilon_0 a_0^3} \sum_{j=1}^{\infty} \sum_{k>j}^{\infty} \frac{x_j x_k}{(k-j)^3} \]

(2.69)

\[ V_y = \frac{m \omega_0^2}{2} \sum_{j=1}^{\infty} y_j^2 + \frac{e^2}{4\epsilon_0 a_0^3} \sum_{j=1}^{\infty} \sum_{k>j}^{\infty} \frac{y_j y_k}{(k-j)^3} \]

(2.70)

\[ V_z = \frac{m \omega_0^2}{2} \sum_{j=1}^{\infty} z_j^2 + \frac{e^2}{4\epsilon_0 a_0^3} \sum_{j=1}^{\infty} \sum_{k>j}^{\infty} \frac{z_j z_k}{(k-j)^3} \]

(2.71)

As a result we can obtain three independent equations of motions for \( x \), \( y \) and \( z \) and the energies we find this way will be additive. Here I will limit myself to the motion in the \( x \)-direction. We find for the equation of motion for the \( j \)th electron

\[ -m \omega_x^2 \ddot{x}_j = -\frac{m \omega_0^2}{2} x_j + \frac{e^2}{2\epsilon_0 a_0^3} \sum_{k=1, k \neq j}^{\infty} \frac{x_k}{|k-j|^3} \]

(2.72)

We can easily obtain a solution when we use the Ansatz \( x_j \sim \exp(iqa_0j) \), from which we find the dispersion relation

\[ \frac{\omega^2(q)}{\omega_0^2} = 1 - 4v \sum_{j=1}^{\infty} \cos(qa_0j) \]

(2.73)

So we see that the dispersion relation depends strongly on the value of \( v \). When we look at the state \( q = 0 \), the dispersion relation reduces to

\[ \frac{\omega^2(0)}{\omega_0^2} = 1 - 4v\zeta(3) \]

(2.74)

where \( \zeta(3) \approx 1.202 \) is the Riemann zeta function. So we see that if \( v \) is larger than

\[ v_{\text{crit}} = \frac{1}{4\zeta(3)} \approx 0.208 \]

(2.75)

\( \omega_x \) becomes complex and the system becomes unstable. This is called the polarization catastrophe. We can also see this from a more physical argument, in which we ignore second-nearest and more distant neighbors in equation 2.69 , and rewrite it in the form

\[ V_x = \frac{m \omega_0^2}{8} \sum_{i=1}^{\infty} [(1 - 4v)(x_i + x_{i+1})^2 + (1 + 4v)(x_i - x_{i+1})^2] \]

(2.76)
We see that if \( v > 1/4 \) than the system can decrease its potential energy by increasing the separation between the electrons to infinity. Therefore we see that the system becomes unstable for \( v > 1/4 \) and the small shift in the critical value for \( v \) is caused by omitting the long-range contributions. So we see that we will have to limit ourselves to the case \( v < v_{\text{crit}} \). However the exact value of \( v_{\text{crit}} \) differs slightly depending on the configuration of the system it was calculated with. If we use for instance an infinite fcc grid instead of an infinite line the value will decrease slightly. An overview of critical values for the most common configurations is given in tabel 2.1 and was obtained from Ref. [10]. So we see that if we want to make sure that no polarization catastrophe occurs in our system we should keep \( v < 0.171 \) and I will usually do this. We know that for silica we have \( v = 0.115 \) and for sapphire \( v = 0.186 \), whereas for metals \( v \) is much higher. As a result I will usually work with silica particles. We see therefore that we can only describe semiconductors with this theory.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>( v_{\text{crit}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>0.208</td>
</tr>
<tr>
<td>Square lattice</td>
<td>0.197</td>
</tr>
<tr>
<td>Simple Cubic</td>
<td>0.187</td>
</tr>
<tr>
<td>Body Centered Cubic</td>
<td>0.183</td>
</tr>
<tr>
<td>Face Centered Cubic</td>
<td>0.171</td>
</tr>
</tbody>
</table>

### 2.6 Discussion

Most of the theory discussed above is not new. The CDM method of calculating the VdW energy between clusters as introduced in section 2.2 was first introduced by Renne and Nijboer in series of articles ([4], [5] and [6]). More recently it has also been discussed in articles by Kim et al., for instance in [1]. Also the calculation of the static polarizability of a cluster is not new. Although it is based on the work by Renne and Nijboer I have not found it in their work. It can however be found in the work by Kim et al. [7]. The method presented in section 2.3 is new, to the best of my knowledge. I am not aware of any earlier work in which an external electric field is included in the Hamiltonian for the VdW interaction. The derivation in section 2.4 I have also not seen before in the literature but the result is given in [10], so this result is also not new. The polarization catastrophe that I described in the last section is a well-known phenomenon and has already been described in the literature [9]. It was however important to describe this phenomena as it limits the range of applicability of our theory. In the following chapters we will see that these well-known models and theoretical ideas can be used to identify a large number of new results.
Chapter 3

Static Polarizability of clusters in an external electric field

In this chapter we will calculate the static polarizability of different clusters in a constant external electric field. We start by investigating cubes and spheres of a finite size. Then we will study what we expect for those clusters in the infinite size limit. As we cannot perform the calculations for large, finite clusters due to limitations on the computing power, we will then investigate a number of approximations, which should allow us to calculate the static polarizability of larger clusters. Then we will investigate the local enhancement factors to see if they can explain why these approximations fail. Next we will try to use the symmetries of the system to reduce the computing power required. At the end of the chapter we will also take a short look at the static polarizability of linear and L-shaped clusters.

3.1 Static polarizability of a finite cube

Here we will use the recipe described in section 2.1 to calculate the enhancement factor of a finite cube. I will do this for different sizes of the cube, where I define $L_{0}$ to be the length of the edge of the cube, so the number of particles in the cube is $N = L^3$. We calculate the enhancement factors from the numerical solutions of equation 2.13. The results are shown in figure 3.1 for two materials (silica ($v = 0.115$) and sapphire ($v = 0.186$)) for $1 \leq L \leq 14$. These results coincide with those by Kim et al. in [7]. We see that the

![Figure 3.1: Enhancement factor of a cube of $N = L^3$ particles. The red dots correspond to sapphire ($v=0.186$) and the blue dots to silica ($v=0.115$).](image-url)
enhancement factor grows with growing size of the cube, but the growth slows down. Therefore there are 2 possible behaviors for even larger cubes: either the enhancement factor converges to a constant value close to the value it has for \( L = 14 \) or it starts to decrease and returns to \( f = 1 \) for very large \( L \). To distinguish between these 2 possibilities we will need to calculate the enhancement factor for larger cubes. However as the computing time required scales with \( L^9 \) and the memory with \( L^6 \), with the current code and computer power I was unable to calculate \( f \) for higher values of \( L \). In this case the memory requirement is the main cause of trouble. Bas Kwaadgras has been able to carry out the calculation until \( L = 18 \) [11] and his results agree with mine. Furthermore he observed a further decrease in the growth of \( f \) but as of yet no decline. In figure 3.2 I investigated the dependence of \( f \) on the value of \( v \) for \( L = 10 \). We note from the left part of this figure that it seems that \( f - 1 \) depends quadratically on \( v \). To further investigate this I plotted the same figure on a logarithmic scale in the right part of figure 3.2 and this confirms that \( f - 1 \) depends, at least approximately, quadratically on \( v \). In the following sections I will investigate the infinite cluster limit as well as methods to approximate the system for larger cubes. However first I will look at the static polarizability of a finite sphere.

### 3.2 Static polarizability of a finite sphere

The calculation of the enhancement factor \( f \) can also be performed numerically for spherical objects. To do this we start by choosing a radius \( R \) for the sphere and then generate either a simple cubic or fcc grid for a cube with an edge-length of at least \( 2R \), such that the sphere fits into the cube, with the origin located in the center. Next we eliminate all particles that are located further than \( R \) from the origin and so we obtain an approximately spherical cluster. Note that for radii small compared to the interparticle spacing \( a_0 \) our clusters can become quite edgy and not necessarily look much like spheres. We can now calculate the enhancement factor numerically and we have done this in three cases, for a simple cubic grid for both sapphire and silica atoms and for an fcc grid only for silica particles. The results are given in figure 3.3. From this figure we notice two important results. First of all, we see that for all but very small spheres (which are not very sphere like as remarked before), the enhancement factor is very close to 1. Furthermore we see that for increasing particle number it decreases to unity. We also note that for very small spheres the behavior is not monotonic. This is probably a result of the way we generated the sphere, as this may create very edgy objects for small particle numbers. Note that I only calculated the case of sapphire particle on a simple cubic grid for large particle numbers as these calculations are very time and memory intensive. As the other two cases had smaller enhancement factors in the range where I did calculate them, I expect them to stay smaller along the entire range. So they would also decrease and could converge to 1. For this calculation the memory requirements are the biggest limitation. The largest calculation I performed consisted of 8217 particles which means that the matrix we work with has \( 607,671,801 \) entries. In our current C++ code this boils down to approximately 4.9 GB of memory needed just to store the matrix. If we compare the
results obtained here with those from the previous section, the result is quite surprising. We note that the enhancement factor of a sphere is much smaller than that of a cube. Furthermore we see that enhancement factor of spheres decreases for larger particle numbers whereas that of cubes keeps increasing. In the next section I will investigate what happens when we look at an infinite cube or sphere.

3.3 Static polarizability of an infinite cube or sphere

Here I will calculate the static polarizability of an infinite cube of particles. As there is no difference between an infinite sized cube and an infinite sized sphere, the result also holds for the latter as long as the particles are distributed along a simple cubic grid. The calculation involves one important assumption based on the infinite size of the cluster. I assume that all particles have equal polarization, i.e. I abolish all surface effects. This polarization I call \( p \). From equation 2.10 we see that

\[
 p' - \alpha_0 \sum_{i=1}^{\infty} T_{i0} p' = e,
\]  

with all symbols as defined in chapter 2. Here we chose \( j = 0 \) meaning that this particle is located in the origin. Next we examine the entries of the matrix \( G = \sum_{i=1}^{\infty} T_{i0} \). We start by looking at the off-diagonal elements of \( G \). I will only calculate \( G^{(1,2)} \) but from symmetry we will see that this result also holds for the other off-diagonal elements. Note that we can write the sum over all particles \( i \) as a sum over the integers \( k \), \( l \), and \( m \) between \(-\infty \) and \( \infty \), where \( k a_0 \) denotes the \( x \)-, \( l a_0 \) the \( y \)- and \( m a_0 \) the \( z \) coordinate of the particle, as long as we exclude that they are not all three allowed to be zero. This then gives (using the form of \( T_{ij} \) from equation 2.6)

\[
 G^{(1,2)} = \sum_{i=1}^{\infty} 3n^{(1)}_{i0} n^{(2)}_{i0} / r_{i0}^3 = \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \frac{3 \cdot k \cdot l}{(k^2 + l^2 + m^2)^{3/2} a_0^3} + \sum_{k=1}^{\infty} \sum_{l=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \frac{3 \cdot k \cdot l}{(k^2 + l^2 + m^2)^{3/2} a_0^3} + \sum_{k=-\infty}^{\infty} \sum_{l=1}^{\infty} \sum_{m=-\infty}^{\infty} \frac{3 \cdot k \cdot l}{(k^2 + l^2 + m^2)^{3/2} a_0^3} = 0,
\]
where in the second line in the sum the case \( k = l = m = 0 \) is excluded. So we see that all off-diagonal elements of \( G \) are zero. Now we turn our attention to the diagonal elements. Again I will only do this for \( G^{(1,1)} \) but the argument is the same for the other cases.

\[
G^{(1,1)} = \sum_{i=1}^{\infty} \frac{3n_{i}^{(1)} n_{i}^{(1)} - 1}{r_{i0}^{3}}
= \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \frac{3k^{2}l^{2}m^{2} - 1}{(k^{2} + l^{2} + m^{2})^{3/2} \alpha_{0}^{3}}
= \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \frac{2k^{2}l^{2} - m^{2}}{(k^{2} + l^{2} + m^{2})^{5/2} \alpha_{0}^{3}} = 0
\]

Here we exclude the case \( k = l = m = 0 \) from the sum. The last equality can be seen as follows. If we have an \( k, l \) and \( m \) such that the numerator is nonzero, then we have 2 more choices of \( k, l \) and \( m \), obtained by interchanging \( k \) and \( l \) and \( k \) and \( m \) respectively, with the same denominator. Furthermore it is easily seen that these 3 terms together give 0 and therefore the entire sum equals 0. So we see that \( G = 0 \) and find from equation 3.1 that

\[
p = \alpha_{\text{atom}} E_{0}.
\]

So we see that we get

\[
f = \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}.
\]

So we find for the enhancement factor of an infinite cube (or sphere) of dipoles on a cubic lattice that \( f = 1 \). However this does not seem to agree with the result in section 3.1, where we saw that the enhancement factor of a finite cube increases with increasing cube size. Here we should however make 2 important notes. First of all we should note that the cubes considered in section 3.1 are relatively small. At \( L = 14 \) still more than 40% of the dipoles is located at the edge of the cluster and therefore to abolish all edge effects seems a bad approximation. Secondly it is doubtful if we can abolish edge effects for any finite cube, because when we sum over the edge we have a 3 dimensional sum of a function that decreases like \( r^{-3} \). Therefore it is not clear what the behavior of \( f \) is for large cubes. In order to investigate this further in the next section we will try to approximate the problem in order to allow calculations of larger clusters.

### 3.4 Approximations

#### 3.4.1 Approximation 1: Dividing a cube into smaller cubes

In this section we will try an approximation which will allow us to calculate enhancement factors for larger cubes. In this way we try to find the behavior of \( f \) for larger cubes than we considered in section 3.1. The approximation consists of dividing the large cube of \( N = L^{3} \) particles into \( N_{2} \) smaller cubes of \( N_{1} = L_{1}^{3} \) particles, such that \( N = N_{1}N_{2} \). We then assume that every small cube of \( N_{1} \) particles can be viewed as a single dipole, with static polarizability equal to that of a cube of \( N_{1} \) particles. Note that even for small values of \( L_{1} \) this can greatly reduce the computing time (which goes with \( N^{3} \)) and memory (which goes with \( N^{2} \)) required. We see that this approximation can only be applied to cubes and not to spheres as there is no way to divide a sphere completely into a number of smaller spheres. Now we can use most of the calculations done in section 2.1, however there will be some small changes. First of all we note that the smaller cubes will have atomic polarizability

\[
\alpha_{\text{small}} = N_{1} f_{1} \alpha_{0},
\]

23
where \( f_1 \) is the enhancement factor of a cube consisting of \( N_1 \) particles. However also the minimal interparticle distance (which will now be equal to the minimal distance between the centers of 2 small clusters) will change to \( a'_0 = L_1 a_0 \) with \( a_0 \) the minimal distance between two particles. This means that the dimensionless interparticle distance \( a \), which is used in the calculations and is connected to the earlier defined \( v \) by 
\[
a = v^{-1/3},
\]
will change. We find that
\[
a_1 = \frac{a'_0}{\sqrt{\alpha_{small}}} = \frac{a}{\sqrt{f_1}},
\]
where \( a \) is the dimensionless distance for single particles (\( a = 2.05 \) for silica particles). Finally equation 2.14 changes into
\[
\alpha_{\text{cluster}}^{(1,1)} = \alpha_{\text{small}} \sum_{j=0}^{N_2-1} \mathcal{P}_{3j+1}
\]
and therefore the enhancement factor becomes
\[
f = \frac{f_1}{N_2} \sum_{j=0}^{N_2-1} \mathcal{P}_{3j+1}.
\]

I have calculated the enhancement factors for silica cubes for \( L_1 = 2 \) and \( L_1 = 3 \) for increasing \( L_2 \) and the results are shown in figure 3.4. We see that this approximation is not very good. Furthermore we note that

if we increase the size of the smaller cube the approximation gets worse. Therefore this approximation does not seem to work and we cannot use it to calculate the enhancement factors for larger cubes.

### 3.4.2 Approximation 2: Hollow Cubes and Spheres

Here I will try another approximation for the static polarizability of large clusters. I will investigate what the effect is of taking hollow clusters instead of filled clusters. We note that for large clusters this could reduce the particle number drastically. I will first consider cubes of \( L^3 \) sites, with lattice spacing \( a_0 \) and atomic polarizability \( \alpha_0 \) for silica, such that the reduced lattice spacing is 
\[
a = \frac{a_0}{\alpha_{atom}^{1/3}} = 2.05.
\]
We fix the
number of layers $n$ of the hollow cube and we notice that if $n < L/2$ the cube is indeed hollow and now only consists of $N = L^3 - (L - 2n)^3 = 6L^2n - 12Ln^2 + 8n^3$ particles instead of the $L^3$ particles in a solid cube. We see that for large $L$, this could greatly reduce the total number of particles and therefore reduce the time and memory the calculations need. I have done the calculations for $n = 1$, $n = 2$ and $n = 3$ and the results are shown in the left part of figure 3.5. Furthermore in the right part figure 3.5 we show $N/L^3$, the number of particles in a hollow cube of $n$ layers as a fraction of the particle number in a solid cube. From this figure we can see how large the reduction in particle number, and therefore in calculation time and memory requirement, would be. We see here clearly that using a hollow cube is a bad approximation as the enhancement factors behavior as a function of $L$ is very different. Even for $n = 3$, $f - 1$ would become almost twice as large for a hollow cube as it is for a solid cube for $L$ as small as 12. We have reduced the particle number here by less than 15%. As the error is very large and the reduction in calculations needed is not, this seems like a bad method to approximate the problem.

Before giving up on this approximation I also consider spheres instead of cubes. To do this I will fix two radii $r_{\text{out}}$, the outer radius, and $r_{\text{in}}$, the inner radius. Note that both are taken in units of $a_0$. Now we generate a simple cubic grid of particles and eliminate all those particles whose distance to the origin is either larger than $r_{\text{out}}$ or smaller than $r_{\text{in}}$. This will give us a spherical shell. Again I will fix $n$, which is now defined as $n = (r_{\text{out}} - r_{\text{in}})/a_0$ and vary $r_{\text{out}}$. We see that this is the maximum number of particles that can be contained in the shell in a straight line from the center of the sphere. Now I work with sapphire parameters, so $a = 1.7518$. The results of the enhancement factor for different $n$ are given in left part of figure 3.6 and the particle fractions in the hollow spheres are given in the right part. We see here clearly that the behavior of a hollow sphere is totally different from that of a solid sphere. For a hollow sphere $f$ is much larger and continues to grow for increasing radius whereas this decreases for a solid sphere. Furthermore for $n = 3$ we only decrease the number of particles by 20%, however $f - 1$ increases by as much as a factor 4. Therefore also this approximation seems to be very bad and useless. So we see that we cannot approximate the enhancement factor of a solid cube or sphere by a hollow one. However, it is interesting to note that hollow objects are so much more polarisable than their solid counterparts. Therefore this part was not completely fruitless.

### 3.5 Local enhancement factors

We have seen in the previous sections that it is hard to approximate the static polarizability of a cube by reducing its degrees of freedom. This would suggest that the size and direction of the atomic polarization $p_j'$ varies strongly in the cube. I will now investigate how these vary spatially throughout the cube. We
study a silica cube with $L = 14$ and fix the electric field in the positive $x$-direction. We now fix the $y$ and $z$
coordinates such that we are in the 8th row and column and investigate how the local enhancement factor
varies when we change the $x$ coordinate. The local enhancement factor $f_j$ is a tensor defined by
\[
p_j = \alpha_0 f_j \cdot E_0.
\] (3.8)

We will examine the different components of this tensor. This is done in figure 3.7. I did not include the $f_{xz}$
component as, due to the symmetry of the cube, this is equal to $f_{xy}$. We note first of all that if we sum over
the right figure, we indeed get 0, so the static polarizability in the cluster will disappear for the off-diagonal
elements. The left part of the figure is more interesting, in comparison to linear and square clusters in figures
4 en 5 in Ref. [7] we do not see the local enhancement factors become (almost) constant, for the inner part
of the cube. Next we look at the same situation but now fix the $x$ and $y$ coordinate at the 8th row and
column and vary the $z$ coordinate (note that the electric field still points in the $x$ direction). This is shown in
figure 3.8. We note that we observe the same behavior as before, i.e. the atomic polarization does not return
to a bulk value quickly, with the exception of the $f_{xy}$ case. If we compare our results with those of Kim
et al. in [7] we note important differences. They only performed the calculations for 1- and 2-dimensional
clusters and their results showed that the atomic polarization returned to the bulk value within 2 or 3 layers.
However we observed that for 3-dimensional objects this does not happen within the first 5 layers and we
need to examine larger clusters to find out if they ever assume a constant bulk value. The reason why the
edge effects seem to play a much more important role in 3-dimensional clusters than they do with lower
dimensional clusters is the following. When we look at the contribution of the edge to the electric field of
a certain particle in the center of the cube, this constitutes a 3-dimensional sum over a function decreasing
as $r^{-3}$. Therefore if we increase the size of the cluster the increased distance to the edge is compensated by
3.6 Exploiting Symmetry

Here I will show how we can use symmetry to reduce the degrees of freedom needed to calculate the static polarizability of a cube. We note that this method was first introduced by Bas Kwaadgras [11]. We know that a cube has several symmetry planes and therefore we expect the polarizations of the individual particles in the cluster also display symmetries. For clarity, from now on the particles will no longer be numbered by a single index, but we will use three indices, denoting their location in the cube. Furthermore, where possible we will abbreviate this as \( n = (n_x, n_y, n_z) \) and instead of \( T_{ij} \) we will now write \( T(n, n') \). In this notation equation 2.10 becomes,

\[
p'(n') - \alpha_0 \sum_n T(n, n') \cdot p'(n) = e. \tag{3.9}
\]

We fix the electric field in the \( x \)-direction. Now we deduce that the main symmetries of the system are:

\[
p'(n_x, -n_y, n_z) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} p'(n_x, n_y, n_z), \tag{3.10}
\]

\[
p'(n_x, n_y, -n_z) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} p'(n_x, n_y, n_z). \tag{3.11}
\]

\[
p'(n_x, n_y, n_z) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} p'(n_x, n_y, n_z). \tag{3.12}
\]
We can combine these to derive more symmetries. This gives us

\[
p'(-n_x, -n_y, n_z) = \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -1
\end{pmatrix} p'(n_x, n_y, n_z),
\]

(3.13)

\[
p'(-n_x, n_y, -n_z) = \begin{pmatrix}
1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 1
\end{pmatrix} p'(n_x, n_y, n_z),
\]

(3.14)

\[
p'(n_x, -n_y, -n_z) = \begin{pmatrix}
1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & -1
\end{pmatrix} p'(n_x, n_y, n_z),
\]

(3.15)

\[
p'(-n_x, -n_y, -n_z) = p'(n_x, n_y, n_z).
\]

(3.16)

We now assume the number of particles on the edge of the box \( L \) to be even and introduce \( l = L/2 \). This allows us to rewrite the sum in equation 3.9 in the form

\[
\sum_n T(n, n') \cdot p'(n) = \sum_{n_x=-l}^{l} \sum_{n_y=-l}^{l} \sum_{n_z=-l}^{l} [T(\{n_x, n_y, n_z\}, n') \cdot p'(n_x, n_y, n_z)]
\]

\[
= \sum_{n_x=-1}^{l} \sum_{n_y=-1}^{l} \sum_{n_z=-1}^{l} [T(\{n_x, n_y, n_z\}, n') \cdot p'(n_x, n_y, n_z)

+ T(\{-n_x, n_y, n_z\}, n') \cdot p'(n_x, -n_y, n_z)

+ T(\{-n_x, -n_y, n_z\}, n') \cdot p'(n_x, n_y, -n_z)]
\]

\[
= \sum_{n_x=-1}^{l} \sum_{n_y=-1}^{l} \sum_{n_z=-1}^{l} [T(\{n_x, n_y, n_z\}, n') \cdot p'(n_x, n_y, n_z)

+ T(\{-n_x, n_y, n_z\}, n') \cdot p'(-n_x, n_y, n_z)

+ T(\{-n_x, -n_y, n_z\}, n') \cdot p'(-n_x, -n_y, n_z)

+ T(\{n_x, -n_y, n_z\}, n') \cdot p'(n_x, -n_y, n_z)

+ T(\{n_x, n_y, -n_z\}, n') \cdot p'(n_x, n_y, -n_z)

+ T(\{-n_x, -n_y, -n_z\}, n') \cdot p'(n_x, -n_y, -n_z)]
\]
where we excluded the \( n_{x,y,z=0} \) case from all the sums. Using the symmetry relations obtained above we can rewrite this into

\[
\sum_n T(n,n') \cdot p'(n) = \sum_{n_x=1}^l \sum_{n_y=1}^l \sum_{n_z=1}^l \left[ \left( T(n_x, n_y, n_z, n') + T(-n_x, -n_y, -n_z, n') \right) \cdot \left( \begin{array}{ccc} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{array} \right) \right] \cdot p'(n_x, n_y, n_z) \\
+ \left[ \left( T(n_x, -n_y, n_z, n') + T(-n_x, n_y, -n_z, n') \right) \cdot \left( \begin{array}{ccc} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{array} \right) \right] \cdot p'(n_x, n_y, n_z) \\
+ \left[ \left( T(n_x, n_y, -n_z, n') + T(-n_x, -n_y, n_z, n') \right) \cdot \left( \begin{array}{ccc} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{array} \right) \right] \cdot p'(n_x, n_y, n_z) \\
+ \left[ \left( T(-n_x, n_y, n_z, n') + T(n_x, -n_y, -n_z, n') \right) \cdot \left( \begin{array}{ccc} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{array} \right) \right] \cdot p'(n_x, n_y, n_z)
\]

where we defined the \( 3 \times 3 \) matrix \( A(n,n') \) by

\[
A(n,n') = T(n_x, n_y, n_z, n') + T(-n_x, -n_y, -n_z, n') \\
+ \left[ \left( T(n_x, -n_y, n_z, n') + T(-n_x, n_y, -n_z, n') \right) \cdot \left( \begin{array}{ccc} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{array} \right) \right] \\
+ \left[ \left( T(n_x, n_y, -n_z, n') + T(-n_x, -n_y, n_z, n') \right) \cdot \left( \begin{array}{ccc} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{array} \right) \right] \\
+ \left[ \left( T(-n_x, n_y, n_z, n') + T(n_x, -n_y, -n_z, n') \right) \cdot \left( \begin{array}{ccc} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{array} \right) \right].
\]

Now we can rewrite the set of linear equations in 3.9 in the form

\[
p'(n') - \alpha_0 \sum_{n_x=1}^l \sum_{n_y=1}^l \sum_{n_z=1}^l A(n,n') \cdot p'(n) = e. \tag{3.17}
\]

We note that we now sum over \( l^3 = L^3/8 \) and have therefore reduced the degrees of freedom in our system with a factor 8. This allows us to investigate much larger systems then before. With this technique Bas Kwaadgras [11] was able to calculate the enhancement factor of cubes up to \( 40 \times 40 \times 40 \) dipoles. The results are shown in figures 3.9 and 3.10. We started by comparing the results we get when we use the symmetry reductions with those obtained without using them. Although there seem to be some small discrepancies between the two lines, this is caused by the fact that the technique using symmetries can only be applied to even values of \( L \). For all even \( L \) both methods give exactly the same answer. Secondly we note that for \( L > 22 \) the enhancement factor is decreasing, although it decreases very slowly. Therefore this might suggest that \( f \) will return to unity for very large \( L \), but this is not yet clear.

### 3.7 Enhancement factors of linear clusters

In this section I will discuss briefly the enhancement factors of linear clusters. We recall from section 2.1 that a linear cluster will have 2 enhancement factors, one corresponding to an electric field parallel to the cluster
and one corresponding to a field orthogonal to the cluster. In figure 3.11 we see the local enhancement factors for linear clusters of increasing size parallel, $f_\parallel$, and perpendicular, $f_\perp$, to the electric field for 3 different materials (silica, sapphire and hexane). Here I used the values for atomic polarizabilities and minimal interparticle distances from table 1 of [7]. We see that there is a clear difference in the behavior of the enhancement factors for the two directions. In particular $f_\parallel$ for the most polarisable substance, sapphire, can be as large as 10 for chains of $\sim 100$ atoms. Furthermore we note that our results here agree very well with those in figure 2 of Ref. [7]. In section 4.2 I will show how the energy of such a linear cluster in an external field depends on the angle of the applied field.

3.8 Static polarizability not parallel to applied field

So far we have only seen static polarizability tensors with all nonzero elements on the diagonal. To illustrate that this is not the only possibility I will now construct a cluster that has nonzero, off-diagonal elements. In fact I will construct a cluster for which all elements of the polarizability tensor are nonzero. We see from section 2.1 that we then must have a cluster which breaks mirror symmetry w.r.t. any plane. We construct the following cluster of particles. We start by placing a particle in the origin. Then we place $L_1 - 1$ particles along the positive $x$-axis, such that we get a chain of $L_1$ particles along this axis, all with the same interparticle spacing. Similarly we place $L_2 - 1$ particles along the positive $y$-axis and $L_3 - 1$ particles along the positive $z$-axis. So we have a line of $L_2$ particles along the $y$-axis and of $L_3$ particles along the $z$-axis.

Now it turns out that if $L_1 > 1$, $L_2 > 1$ and $L_3 > 1$ then all components of our static polarizability tensor $\alpha_{\text{cluster}}$ are nonzero. For instance for silica parameters (a=2.05) and $L_1 = 10$, $L_2 = 9$ and $L_3 = 6$ we find for the enhancement factor tensor $f$,

$$
\mathbf{f} = \begin{pmatrix}
1.30755 & -0.025479 & -0.023459 \\
-0.025479 & 1.2441 & -0.0232655 \\
-0.023459 & -0.0232655 & 1.22944
\end{pmatrix}.
$$

(3.18)

Clearly, it is symmetric and can thus be diagonalized. If we apply an external electric field along any of the eigenvectors we will find a static polarization parallel to that applied field and the size of the enhancement factor will be equal to the corresponding eigenvalue of $\mathbf{f}$.
3.9 Discussion

We investigated the enhancement factors of both finite and infinite cubic and spherical clusters. In Ref. [7] the authors give the result for the static polarizability for an infinite cube without giving the full calculation. However they also give results for other kinds of infinite clusters and only perform the calculation for one case, that of an infinite line. My calculation in section 3.3 is based on this calculation. In the same article the authors also give results for the static polarizability of a finite cube. However they only give results up to $L = 10$, although they say to have investigated cubes up to the size of $L = 17$. Their results agree very well with those shown in section 3.1. They also claim to have investigated spherical clusters up to 5000 particles in size, but as they have not presented any results of this I can not compare this to my results in section 3.2. The approximations in sections 3.4.1 and 3.4.2 I have not seen in the literature before. However as they both work very badly, this is not surprising. Local enhancement factors were already calculated in [7] as well, however the case of a cubic cluster was not studied there. The authors did study the local enhancement factors of a square and their results differ quite strongly from my result for cubes. The main difference is that in squares the local enhancement factor is constant in the middle of the square whereas that of cubes is not. The use of symmetry to reduce the degrees of freedom for the cube, was first introduced by Kwaadgras [11]. The results for linear clusters given in section 3.7 are not new either. They were given in the same
article by Kim et al. as I mentioned before and my results seem to agree very well with the authors. The L-shaped clusters discussed in the previous section I have not seen before in the literature, but this is not very surprising as these clusters are not the most interesting. I only used them to illustrate that not all clusters need to have a diagonal static polarizability matrix. So to conclude the results in sections 3.4.1, 3.4.2 and 3.7 are new results whereas the others are not.
Chapter 4

VdW interactions between two clusters in vacuum

In this chapter I will start to look at the interactions between two nanoclusters. Here I will only concern myself with clusters consisting of 1 type of particles in vacuum. In the next chapter I will discuss some clusters consisting of multiple types of particles and in chapter 6 I will show a number of methods to introduce a solvent in our system. The layout of this chapter is as follows. In the first section I will reproduce some of the results on dimer and decamer interactions as shown by Kim et al. in [1], where I will mainly focus on the anisotropy of this interaction. Next I will investigate if an external electric field changes this interaction at all. In section 4.3 I will compare the interaction between spheres with the pairwise sum method, which is the most commonly used method in literature to calculate the VdW interaction between clusters. Next I will investigate if it is energetically favorable to form chains of clusters and the results are presented in section 4.4. In section 4.5 I will show a surprising result on the interaction strength between linear clusters and their length. I will end the chapter with a discussion.

4.1 Reproduction of literature results for dimers and decamers

In this section I will research the interactions between linear clusters in the absence of an external electric field. We will see that the results agree with those of Kim et al. [1]. The clusters that we use will be made of silica, which means that $v = 0.115$ and $\omega_0 = 2.033 \times 10^{16} \text{s}^{-1}$. We will study the interaction between two dimers as well as between two decamers. A dimer is a linear cluster consisting of 2 particles and a decamer is one consisting of 10 particles. I investigate two possible orientations for the linear clusters, $zz$ and $xx$. Here the $zz$ orientation denotes a head to tale orientation whereas $xx$ denotes a parallel orientation, see figure 4.1. In figure 4.2 we see the interaction energy, as defined in equation 2.32, as a function of the center to center distance $r$ between the clusters. We see that the attractive force between the particles falls of very rapidly with increasing $r$. In order to compare our results with those in the literature I also calculated the

\[ E(r) = k \left( \frac{1}{r} - \frac{1}{2r^2} \right) \]

where $k$ is the spring constant and $r$ is the center to center distance. The results are shown in figure 4.3 and we see that our results agree well with those of Kim et al. [1].
anisotropy ratio $V_{zz}/V_{xx}$ for both dimers and decamers. In figure 4.3 we see the result and we see that it agrees perfectly with that in figure 1 of Ref. [1]. However we note that this is way of presenting the result is suggesting that the most energetically favorable position is in the $zz$ orientation, but from figure 4.2 we see that this is clearly not the case. The difference is caused by the fact that in the $xx$ orientation the clusters can get much closer than in the $zz$ orientation and this is not conveyed in figure 4.3. We do note that the interaction depends strongly on the orientation of the cluster. In the next section I will study how this interaction changes when we include an external electric field.

4.2 Influence of external electric field on interactions

Here I will study the influence of an external electric field on the interaction between clusters. I start by examining how the potential energy of 1 cluster depends on its orientation in the electric field. We recall that if the static polarization of the cluster is a multiple of the identity matrix, then the energy is independent of its orientation. Therefore I consider here a linear cluster, for which we know from section 3.7 that its static polarization is not a multiple of the identity matrix and its energy is as a result orientation dependent. The results are shown in figure 4.4 for a linear cluster of 10 particles as a function of the angle $\theta$ between the cluster orientation and the external electric field. In the left part we see the energy due to the external field for a range of materials, where I divided out the strength of the external electric field. In the right part I fixed the field strength at $E_0 = 3 \times 10^6 \text{V/m}$ and the material to be silica, and plotted the energy in units of $kT$. Here I only investigated the magnitude of the second term in equation 2.53, so it only shows the magnitude of the contribution of the electric field. Note that both terms in this equation 2.53 are positive so the adding of the electric field always lowers the potential energy of the cluster. Furthermore we see that increasing $v$ means an increase in the interaction with the electric field, but the functional form of the dependence on $\theta$.
does not seem to be affected by it. Note that the correction term shrinks with increasing angle so we see

\[ \frac{2 V_{\text{int}}^E}{\hbar \omega_0} \delta^2 \]

and the lines from bottom to top correspond to \( \theta = 0, \theta = \pi/6, \theta = \pi/4, \theta = \pi/3, \theta = 4\pi/10, \theta = 9\pi/20 \) and \( \theta = \pi/2 \).

that the potential energy is the lowest if the electric field is parallel to the decamer. Furthermore we see

that the influence of the external electric field on the energy of one cluster is very small as it is of the order \( 10^{-7}kT \).

Next we consider the interaction between 2 decamers in an electric field in the \( zz \)-orientation (head to tail). We will examine the dependence of the interaction on the angle of the electric field. I have done this in figure 4.5 and now I have plotted the interaction energy as a function of the electric field strength in the units of \( \tilde{E} \) as defined in equation 2.52, where the different colored lines represent different angles with the electric field and I fixed the center to center distance at \( r = 20a \). We see that the interaction energy

\[ \frac{2 V_{\text{int}}}{\hbar \omega_0} \]

increases with the magnitude of the electric field for all angles smaller than \( \theta = 4\pi/10 \) and decreases above these angles.

However if we want to better understand the strength of the forces and the importance of the correction term due to the electric field we will have to work with more familiar units. If we use that \( \hbar = 1.05 \times 10^{-34} \text{m}^2 \text{kg} \), \( \alpha_0 = 5.25 \times 10^{-30} \text{m}^3 \), \( \omega_0 = 2.03 \times 10^{16} \text{Hz} \) and \( \epsilon_0 = 8.85 \times 10^{-12} \text{C}^2/\text{m}^2 \text{kg} \) we find that

\[ \mathcal{E} = 2.14 \times 10^{11} \frac{V}{m} \]  

(4.1)
As we know that the dielectric field strength of air is approximately $3.0 \times 10^6 \text{V/m}$ we see that the largest values of the electric field plotted in figure 4.5 already exceed this. Therefore I now examine the behavior of the interaction energy as function of the distance between the clusters for an electric field equal in strength to the dielectric field strength in air. Furthermore I have rescaled the vertical axis to denote the energy in $kT$. All this is done in figure 4.6 for the electric field oriented along the clusters. First of all I want to point out that if we also plot the energy with the electric field oriented perpendicular to the clusters the lines are exactly on top of each other everywhere and therefore the effect of the electric field seems negligible. If we compare this result with that in figure 4.2, we also see that they agree perfectly and this supports our conclusion that the effect of an external electric field is negligible. When $r < 50a_0$ the effect of the electric field is always smaller than 0.1%. However the effect does grow with increasing distance but we should note here that as our current theory does not take retardation into account it is only valid for $r < 10\text{nm}$ and in this range the effect is negligible. Therefore from now on I will no longer take an external electric field into consideration.

### 4.3 Comparison to pairwise sum method

In this section I will compare the interaction energy as obtained from the CDM method with that of the pairwise sum method, which is often used in literature as it is very easy to use. The pairwise sum method gives the interaction energy $V$ as the summation over two-body interactions $V_{ij}$ between all atoms $i$ in cluster A and atoms $j$ in cluster B:

$$V = \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} V_{ij} = -\sum_{i=1}^{N_A} \sum_{j=1}^{N_B} \frac{C}{r_{ij}^6}. \quad (4.2)$$

Here $C$ is a constant that governs the strength of the interaction and which is related to the well known Hamaker constant $A$ by $A = \pi^2 n^2 C$, where $n$ is the number density of the cluster [8]. It is clear that any result will depend directly on the Hamaker constant, for which unfortunately different values exist in literature. In Ref. [8] two different methods of calculating this constant are given. First it is assumed that

$$A_{\text{sum}}^{(jk)}(i\omega) = 3\pi n^2 \hbar \int_0^\infty \alpha^{(j)}(i\omega)\alpha^{(k)}(i\omega)d\omega, \quad (4.3)$$

where $\alpha^{(j)}(i\omega)$ is the polarizability of atom $j$ at imaginary frequency $i\omega$, $j$ and $k$ denote different particle species and the subscript sum is taken in accordance to [8] to show the difference with other methods of
calculating $A$. Assuming that all atoms are of the same type and using the Drude model, i.e.

$$\alpha^{(i)}(i\omega) = \frac{\alpha_0^{(i)}(\omega_0^{(i)})^2}{(\omega_0^{(i)})^2 + \omega^2},$$  \hspace{1cm} (4.4)

one finds, assuming that there is only one species of particles (with parameters $\alpha_0$ and $\omega_0$)

$$A_{\text{sum}} = \frac{3\pi^2\hbar \omega_0 n^2 \alpha_0^2}{4}. \hspace{1cm} (4.5)$$

We see that this gives the same value for $C$ as we obtained from the CDM calculation for 2 particles in equation 2.39. Kim et al. also perform a second calculation of the Hamaker constant based on Lifshitz theory, which starts with

$$A_{DLP} = \frac{3\hbar}{4\pi} \int_0^\infty \frac{(\epsilon(i\omega) - 1)}{(\epsilon(i\omega) + 1)^2} d\omega, \hspace{1cm} (4.6)$$

where $\epsilon(i\omega)$ is the dielectric response function of the material and the subscript DLP was again chosen in accordance to [8] and stands for the Dzyaloshinskii-Lifshitz-Pitaevskii approach, which is often referred to as Lifshitz theory. They proceed by using the Clausius-Mossotti relation,

$$\frac{4\pi \alpha(i\omega)}{3} = \frac{\epsilon(i\omega) - 1}{\epsilon(i\omega) + 2}, \hspace{1cm} (4.7)$$

and the Drude model to show that

$$A_{DLP} = \frac{3\pi^2\hbar \omega_0 n^2 \alpha_0^2}{4(1 + 2\pi n \alpha_0/3)^{3/2}}. \hspace{1cm} (4.8)$$

We note that

$$A_{DLP} = \frac{A_{\text{sum}}}{(1 + 2\pi n \alpha_0/3)^{3/2}}. \hspace{1cm} (4.9)$$

and therefore $A_{\text{sum}} > A_{DLP}$. For silica we find that $A_{\text{sum}} = 20.99 \times 10^{-20} J$ and $A_{DLP} = 15.18 \times 10^{-20} J$. If we compare the results from CDM with the results from the pairwise sum with these Hamaker constants as done in figure 4.7 we see that they agree quite well. Here I plotted the ratio of the pairwise method to the CDM method, which is defined as $R = V_{\text{sum}}/V_{\text{CDM}}$. We note first of all that the calculation with $A_{\text{sum}}$ agrees better with the CDM result than that $A_{DLP}$ does. However we do see that for increasing particle size the difference between $A_{\text{sum}}$ and CDM increases whereas that between $A_{DLP}$ and CDM decreases. This is especially the case for short separations between the spheres. In figure 2 of Ref. [8] the authors plotted the same result for spheres of 2340 particles and we see there that for short separations $A_{DLP}$ gives a better approximation than $A_{\text{sum}}$. Unfortunately because of computational problems I cannot reproduce the calculations for this size of particle. The calculations on the spheres of 1481 particles took approximately 40 hours to complete on the Venus server using 14% of its memory. As computational time increases with $N^3$ and memory by $N^2$ a calculation on spheres of 2340 particles would take more than 135 hours and require more than 31% of the total memory of Venus. Therefore I have not performed this calculation. However $A_{\text{sum}}$ and $A_{DLP}$ are not the only values for the Hamaker constant for silica used in the literature. For instance Bergstrom [12] finds from experimental data the value $A_{\text{Berg}} = 6.50 \times 10^{-20} J$ and this value also appears in other literature. Therefore I also drew the line corresponding to this value in figure 4.7 and we see that this does not agree very well with the CDM result. This could be expected as the interaction energy scales linearly with the Hamaker constant. We conclude that the result of the pairwise sum depends on the value of the Hamaker constant that is used and that there is quite a large spread in the values given
in the literature. However we also see that as the Hamaker constant influences the interaction potential only linearly the behavior of the energy calculated from the pairwise sum is almost the same as that from the CDM model. Therefore if we choose our Hamaker constant in such a way that at large distances this gives the same value as the CDM model we expect it also to be a good approximation at smaller separations. This can be seen from the left part of figure 4.7 where the $A_{\text{sum}}$ calculation approaches the CDM value for large separations and is about 10% off for the small separations. For the smaller spherical clusters this is about $0.5kT$ whereas for the larger spheres this is about $2kT$. So we can conclude that the pairwise sum method can be a good approximation, especially given the time it can save in calculations, as long as the correct value for the Hamaker constant is used. However it seems that the value of the Hamaker constant which best approaches the CDM value will depend on the size and possibly shape of the clusters and therefore we see that many body effects are important.

4.4 Chain formation

4.4.1 Atoms

In this section I will use the CDM method to investigate if it is energetically favorable for clusters of particles to form chains as opposed to less organized groupings. To do this I will start with two clusters next to each other on a line (so they form one large cluster) and then see if for a third cluster it can lower its potential energy by moving onto the end of the cluster on that same line as opposed to joining the cluster from another position. The two positions which would intuitively have lowest potential energy are shown in figure 4.8 for spherical clusters. I will start by looking at clusters consisting of only 1 particle. For now I fix $a = \frac{a_0}{\alpha_{\text{atom}}} = 2$

![Figure 4.8: Two orientations for 3 spherical clusters](image)

but later I will also look at a different value. The interaction energy now only depends on 2 parameters, the distance $r$ between the centers of the 2 clusters and the angle $\theta$ between the line on which the two particles in the first cluster lie and the line connecting the centers of the clusters, see figure 4.9. First we fix $r$ and look at the dependence on $\theta$. This is done in figure 4.10 in the green line. Here I illustrated the situation for
Figure 4.9: The 3-particle geometry of interest with two particles at contact and a third one at separation \( r \) from the contact point and at an angle \( \theta \).

Figure 4.10: Dependence of interaction energy of adding a particle to a line of \( N \) particles on \( \theta \) for \( r \) such that the extra particle just touches the line for \( \theta = 0 \). The colors correspond to \( N = 2 \) for green, \( N = 3 \) for blue, \( N = 4 \) for red, \( N = 5 \) for yellow and \( N = 10 \) for pink.

\( r = 1.5a_0 \) in which case for \( \theta = 0 \) the two clusters are just touching. The other colored lines correspond to longer initial chains of 3, 4, 5 and 10 particles respectively. Here \( r \) is still the distance between the centers of the two clusters and is chosen in such a way that the two clusters line up for \( \theta = 0 \). I have also looked at other distances but the behavior is similar (it is not possible to show this in the same plot due to large differences in the energy). We now clearly see that the interaction is strongest for \( \theta = 0 \) and \( \theta = \pi \), so that it appears that the third particle would fall in line with the other two. However closer inspection shows that the minimum in the potential observed can only be a local minimum as we can see when we look at figure 4.11, where I plotted the interaction energy as a function of the distance \( r \) for \( \theta = \pi/2 \) fixed. Note first of all that for this angle \( r \) can become much smaller than the minimal distance used in the previous plot and as a result of that the interaction can become more attractive. So we see that the minimum at the end of the chain is not a global minimum. To investigate if it is at least a local minimum we now consider a different parametrization of the system as given in figure 4.12. By using this new parametrization we can now see what happens when we keep the new particle fixed to the existing cluster, but let it slide along the edge of the outermost particle. The results for \( a = 2.0 \) and \( a = 1.7 \) are shown in figures 4.13 and 4.14. We see that there is indeed a local minimum at the end of the chain. Furthermore for \( a = 1.7 \) we see that the particles have to overcome a potential barrier of a several \( kT \) to get to the global minimum, so this could support chain formation. Finally we also notice that the barrier becomes larger if the chain size increases, so a small chain can grow larger.
1.2 1.4 1.6 1.8 \( r \)
-12
-10
-8
-6
-4
-2
V HkT L

Figure 4.11: Dependence of interaction energy of adding a particle to a line of \( N \) particles on \( r \) for \( \theta = \pi/2 \). The colors correspond to \( N = 2 \) for green, \( N = 3 \) for blue, \( N = 4 \) for red, \( N = 5 \) for yellow and \( N = 10 \) for pink.

Figure 4.12: Redefinition of parameters for the 3-particle geometry of interest with two particles at contact and a third one at separation \( r \) from the contact point and at an angle \( \theta \).

4.4.2 Cubic Clusters

Next we can repeat the calculation but now with the single particles interchanged by cubic clusters with \( L \) particles on the edge separated by the lattice spacing \( a_0 \). I will only do this for the case of 3 clusters, two lined up and close together forming one \( 2L \times L \times L \) cluster and a third cluster joining them. I will illustrate this for clusters with \( L = 5 \) but the results are qualitatively the same for other \( L \) (although I have only investigated up to \( L = 7 \)). As we now have cubic particles I will use cartesian coordinates instead of the polar coordinates used before. The orientation of the system is given in figure 4.15. I will now illustrate two cases, both for \( a = \sqrt[3]{1/v} = 2.0 \). First I fix \( x = 7.5a_0 \), such that the third cluster can just slide past the other two on the right side and vary the value of \( y \). Note that this means that when \( y = 0 \) all three clusters lie on the same line. The result is shown in figure 4.16. We directly notice that, as expected, our system is symmetric in \( y = 0 \). For positive \( y \) we see that we have 5 points which are either local minima or where the slope flattens drastically. These points are located at \( y = 0, 1, 2, 3, 4a_0 \) and can be easily explained. At \( y = 4 \), the bottom row of particles from the third cluster aligns exactly with the top row of the other two, thereby minimizing distance between the closest particles and increasing the interaction. At \( y = 3 \) the bottom 2 rows line up with the top 2 lines and this continues until at \( y = 0 \) all 5 rows are lined up. Similar behavior is observed when we fix \( y = 5 \) and vary \( x \), i.e. we slide the third cluster along the top of the other two. The result is shown in figure 4.17. We see a situation very similar to that depicted in figure 4.16. Now we have 6 minima of almost equal value in the middle, corresponding to all the configurations where all five columns of the third cube align with those of the large cluster. As \( x \) increases we see that we still can clearly make out the points where either 4, 3, 2 or 1 column aligns with the large cluster. From figures 4.17 and 4.16 we can also see that the global minimum is not located at \( (x, y) = (7.5, 0) \). In other words lining up is not the energetically most favorable configuration. However the difference in energy with the global minimum is only
about $15kT$ whereas the barrier in between the two is of the order of $200kT$. So once formed a chain should be pretty stable. Here I would like to point out that calculations on chain formation for spherical clusters have also been performed [11] and these results agree with those above. It is found that chain formation is never the energetically most favorable state and that there is a barrier that a particle has to overcome when passing from the end of the chain to the most favorable position.

### 4.5 Interaction as function of particle number

We observed an interesting phenomenon when we increase the number of atoms in the clusters whilst keeping the minimal separation $l$ between the clusters constant. We study linear clusters in different orientations. Although this cannot be easily tested experimentally I still present this result here as it is counter intuitive and therefore surprising. First of all if we do this with 2 linear particles that are parallel (so xx orientation) we observe linear growth of the interaction energy as seen in figure 4.18. This is what one would naively expect and is therefore not very interesting. However if we move to the two orientations given in figure 4.19, namely zz and xz orientation the picture becomes very different as shown in figures 4.20 and 4.21. We now see to our surprise that the attraction energy does not increase with increasing atom number. Depending on the separation $l$ it either first increases and then decreases rapidly or directly starts decreasing with increasing $N$. Although a priori this might not be expected there is a good explanation for this behavior. To see this we look at a zz oriented pair of clusters A and B both consisting of $N$ atoms. If we now double $N$ whilst keeping $l$ fixed we see that this corresponds to placing a new cluster C directly adjacent to A and a cluster D adjacent to B. If the atom number is large enough, then due to the length of the clusters...
Figure 4.15: Orientation of the system of interest for 3 cubic clusters of which 2 are lined up and the third is a distance \((x, y)\) away.

Figure 4.16: Interaction potential for 3 cubic clusters of 125 particles each with lattice spacing \(a_0\) and \(a = 2.0\) as function of the \(y\)-coordinate of the third cluster for \(x = 7.5a_0\).

Cluster C will not interact very strongly with cluster B and similarly for clusters A and D. However, cluster C does interact strongly with cluster A and therefore pulls it away from cluster B and similarly for cluster D. Therefore, the total attraction energy will start to decrease if the particle number is so large that cluster C pulls on cluster A harder than it pulls on clusters B and D combined. It is also clear why this behavior is not observed in the \(xx\) orientation.

4.6 Discussion

We have seen how the interaction between linear clusters depends on their orientation. As mentioned above, the results in section 4.1 agree with results obtained earlier by Kim et al. in [1]. We extended the method to investigate the influence of an external electric field on the interactions between decamers and found it to be negligible for electric fields that we can currently achieve in experiments. To the best of my knowledge, no one has ever examined the effects of an external electric field on the interactions according to the CDM model. This means therefore that the results in section 4.2 as well as the conclusion that a constant external field has no influence on the interactions are new. Next, we compared the results from the CDM for spherical particles with those from the two particle sum. We found that the difference between the results is about 20\%, however this does depend on the value of the Hamaker constant used in the two particle sum. These results have also been obtained by Kim et al. before [8]. In section 4.4 we examined if chain formation is energetically favorable and found this not to be the case. In the literature, I have not yet found a study of possible chain formation using the CDM model. Most sources, see for instance Ref. [13], use clusters consisting of metallic particles (possibly capped to prevent aggregation) which cannot be described by the CDM model. Therefore, I conclude that these results are also new. We concluded the chapter with an
Figure 4.17: Interaction potential for 3 cubic clusters of 125 particles each with lattice spacing \( a_0 \) and \( a = 2.0 \) as function of the \( x \)-coordinate of the third cluster for \( y = 5a_0 \).

Figure 4.18: Van der Waals potential energy for 2 linear clusters of silica particles in \( xx \) orientation as a function of the particle number \( N \) at a minimal separation \( l = 5a_0 \).

investigation of the relation between the length of linear chains and their interaction energy. Surprisingly we found that, when the chains are not parallel, the interaction energy decreases with longer chains. This result is also, to the best of my knowledge, not obtained before. So we see that we have been able to reproduce a number of the most important results of Kim et al. as well as obtain new results. To do this we only slightly extended the theory to encompass an external electric field, but all the results, with exception of those in section 4.2, have been obtained with the standard theory. It is therefore very promising that we could still obtain so many new results with this theory.
Figure 4.19: Orientation of the clusters

Figure 4.20: Van der Waals potential energy for 2 linear clusters of silica particles in $zz$ orientation as a function of the particle number $N$ at a minimal separation $l = 3a_0$ (top left), $l = 5a_0$ (top right), $l = 10a_0$ (bottom left) and $l = 20a_0$
Figure 4.21: Van der Waals potential energy for 2 linear clusters of silica particles in $zx$ orientation as a function of the particle number $N$ at a minimal separation $l = 3a_0$ (top left), $l = 5a_0$ (top right) and $l = 10a_0$ (bottom)
Chapter 5

Interactions between capped spheres

We saw in the previous chapter that as the VdW interaction is always attractive, 2 clusters prefer to be as close together as possible. This means that they aggregate if we were to dissolve them into a solvent. To prevent this, experimentalists often cap their particles with a brushlike layer of apolar molecules, e.a. organic polymers. The steric interactions between the brushes then provide a repulsive force to counteract the VdW attraction and prevent aggregation. In this chapter I will try to model spheres with a capping layer using the CDM method. In the first paragraph I will describe the theory of steric interactions.

5.1 Steric Interactions

Steric interactions occur when the outer layers of particles capped with a layer of brushes overlap as a result of the decreasing volume that is available for each individual brush. Here I will describe a model to calculate these interactions and as reference I will use both an unpublished report by Laura Fillion and the book by Israelachvili [14]. The model I will be using is the Alexander-de Gennes model, named after Alexander and de Gennes who showed that the repulsive force per unit area of two infinite parallel plates covered with brushes is given by the pressure [14]

\[
P(d) = \frac{kT}{s^3} \left[ \left( \frac{2L}{d} \right)^{9/4} - \left( \frac{d}{2L} \right)^{3/4} \right],
\]

for \( d < 2L \), where \( d \) is the separation between the plates, \( L \) is the brush thickness and \( s \) is the mean distance between polymers on the surface. We now use the so-called Dejaguin approximation to relate this to a force between capped spheres. This approximation states that the force \( F_c(d) \) between two curved surfaces can be related to the interaction free energy between two planar surfaces \( W(d) \) by

\[
F_c(d) \approx 2\pi R^* W(d),
\]

where \( R^* \) is the combined curvature of the two surfaces given by

\[
R^* = \frac{R_1 R_2}{R_1 + R_2},
\]

with \( R_i \) the radius of particle \( i \). From equation 5.1 we find that the interaction energy per unit area, defined as \( W(d) = \int_{\infty}^{d} dx P(x) \), is given by

\[
\beta W(d) = \frac{8L}{35s^3} \left[ 7 \left( \frac{2L}{d} \right)^{5/4} + 5 \left( \frac{d}{2L} \right)^{7/4} - 12 \right].
\]
Now it is an easy exercise to derive from equation 5.2 that the steric interaction between capped spheres of radii \( R_1 \) and \( R_2 \) at a center to center distance \( r = d + R_1 + R_2 \), is given by

\[
V_{\text{steric}} = \frac{32\pi R_1^3 L^2}{35 s^3} \left[ 28 \left( x^{-1/4} - 1 \right) + \frac{20}{11} \left( 1 - x^{11/4} \right) + 12(x - 1) \right],
\]  

(5.5)

where \( x = (r - R_1 - R_2)/(2L) \). Note that the De-Gennes model is only valid if \( d < 2L \) so if \( r < 2L + R_1 + R_2 \) and therefore we have that \( x < 1 \). If \( r > 2L + R_1 + R_2 \) the capping layers of the spheres do not overlap and there is no steric interaction. Here I will only work with spheres for which \( R_2 = R_1 = R \) and in this case equation 5.5 reduces to

\[
V_{\text{steric}} = \frac{16\pi R L^2}{35 s^3} \left[ 28 \left( x^{-1/4} - 1 \right) + \frac{20}{11} \left( 1 - x^{11/4} \right) + 12(x - 1) \right].
\]  

(5.6)

To get a feel for the behavior of this force I plotted the part between the brackets in figure 5.1. We see that the steric interaction reduces to 0 for \( x = 1 \) and is strongly repulsive for \( x < 1 \). Therefore it is a suitable candidate to prevent aggregation.

5.2 Description of Model

Now that we know how to calculate steric interactions we can calculate the interaction energy between 2 capped clusters. Our clusters consist of a spherical core of \( N_c \) particles of type 1. Like before, these particles are placed on an fcc grid and all particles which are located further than \( r_{\text{core}} \) from the origin are removed. This gives us an approximate sphere with an fcc structure. The particles in the core are defined by 3 parameters: their static polarizability \( \alpha^{(1)}_0 \), interparticle separation \( a^{(1)}_0 \) and characteristic frequency \( \omega^{(1)}_0 \). Note that I demand that the entire core is located within a sphere of radius \( r_{\text{core}} \) around the origin, so this means that the largest distance a particle center is allowed to have is \( r_{\text{core}} - a^{(1)}_0 /2 \). On these spheres we will place brushes consisting of particles of type 2 and defined by the parameters \( \alpha^{(2)}_0, a^{(2)}_0 \) and \( \omega^{(2)}_0 \). We fix every brush to consist of \( n \) particles, and the number of brushes on a cluster is denoted by \( N_b \). We now proceed to place the bases of the brushes. We place them on a sphere of radius \( r_{\text{core}} + a_2/2 \) around the origin. The brush bases are placed using a spiral division using the golden section. This is an easy and fast method to place them approximately evenly distributed along the sphere, which lacks the symmetry of some of the other methods, but is accurate enough for our purposes. The code I used to do this can be found in Ref. [15]. Now we proceed to place the rest of the brushes. We place the second particle of the brush under an angle \( \theta \) with the line between the first particle and the origin. This angle \( \theta \) will be determined by using a Gaussian distribution with fixed variation called the flexibility. We then repeat this process until all \( n \) particles of all \( N_b \) brushes are placed. Note that a high flexibility will mean that the brushes can bend very
easily whereas a flexibility of 0 means they can not bend at all. I put some restrictions on the placement of the brush particles such that they cannot overlap with any core particles or any brush particles already placed. If this happens the algorithm picks a new angle $\theta$ until no overlap occurs. If it turns out to be impossible to do this I reject the setup and start over. In this way I generate the first of the two clusters. For the second cluster there are some small differences. I start by placing the cluster core at a distance $r$ from the origin. Then I check if I can place all the brush bases. This is not always possible as it can happen that a brush particle of cluster 1 is in the way of a base particle of cluster 2. If this happens the calculation for this setup is aborted here and we start over. If all the brush base particles of cluster 2 can be placed, we proceed by placing the other brush particles in a similar method as before. If this means that it is impossible to place all the brush particles of cluster 2, for instance when we have a very large number of hairs or they are very stiff, the calculation will be aborted again. Otherwise the setup is now completed. An example of a correct nonoverlapping setup is shown in figure 5.2. The interaction energy now consists of two parts.

Figure 5.2: Setup of the system for with $N_c = 79$ core particles, $N_b = 50$ brushes and $n = 8$ particles per brush.

A negative Van-der-Waals energy, which is calculated using the theory in section 2.4 and a positive steric energy following from the calculation is the previous section.

5.3 Discussion of parameters

Our model depends on a large number of parameters. The first 6 correspond to the polarizability, size and characteristic frequency for each type of particle we use. Furthermore we have the number of particles in the core, $N_c$, the number of brushes $N_b$ and the number of particles $n$ in each brush. We also have to fix the flexibility of the brushes and can then calculate the interaction energy as a function of the separation $r$ between the clusters. However in order to do this we still have to express both the mean distance between the brushes $s$ and the brush thickness $L$ in the other parameters. First I will show how to calculate $s$. The brushes are attached to a sphere of radius $r_{\text{core}}$. On average the area to which one base is attached is then given by $A = 4\pi r_{\text{core}}^2/N_b = \pi s^2$, where $s$ is the diameter of the effective circular area per bas, yielding

$$s = 4r_{\text{core}} \sqrt{N_b}.$$  \hfill (5.7)

The calculation of $L$ is less clear. Naively one could think that the brush thickness is equal to the contour length of a single brush, so $L = na_0^{(2)}$. However as the brushes usually bend easily this would be an overestimate. In the book by Israelachvili [14] the author gives an expression for $L$, but this is only valid
in what he calls a "good solvent", which is as a solvent in which the different brush segments repel each other. In our model this is not the case. As the system is considered to be in vacuum and the only force between the different brush segments is the attractive VdW force, we would have a bad solvent according to Israelachvili. The relation he derives for a good solvent is

\[ L = \frac{n \left( a_0^{(2)} \right)^{5/3}}{s^{2/3}}. \]  

As this relation is not valid in vacuum and furthermore I think that the flexibility of the polymers should also be taken into account, I will treat \( L \) also as a free parameter.

Now we need to fix values for all parameters. I choose to put 135 silica particles in the core, so this fixes \( N_c = 135, a_0^{(1)} = 5.25 \text{Å}^3, a_0^{(1)} = 3.569 \text{Å} \) and \( \omega_0^{(1)} = 2.033 \times 10^{16} \text{s}^{-1}. \) However it is not so easy to fix the parameters for the brush particles as I cannot find many useful data in the literature. In ref [13] they use \( a_0^{(2)} = 1.2 \text{Å}, \) which I will use here. However I have been unable to find values for \( a_0^{(2)} \) and \( \omega_0^{(2)} \). Neither did I find any data on values for the flexibility nor for the brush thickness. Furthermore it makes sense to both vary the number of brushes \( N_b \) and the number of particles in the brushes \( n \). So we see that we still have 6 undetermined parameters. As the calculations are quite lengthy due to the large particle number as a result of including the brush particles and we need to repeat them many times in order to average out the affect of the random placement of the brushes, I have not investigated how the behavior of the system depends on all the parameters. However, there are only 2 possible behaviors for the system. Either the steric interaction is too weak to counter the VdW attraction and we still have aggregation, or it is strong enough and the interaction potential will have a minimum located further away than the minimal separation between the spheres. In figure 5.3 we see the interaction energy for \( r = 23 \text{Å} \), whereas the red line gives the interaction energy between 2 noncapped spheres. To create these plots I averaged over 40 system setups in every data point (located 0.5 Å apart). However as many system setups were rejected (especially for small \( r \)), in some points as few as 8 useful data points were obtained.
5.4 Discussion

The model presented in this section and all the results are new. As far as I can tell no one has ever applied the CDM method to capped particles before. Unfortunately due to the large number of parameters involved, I have not been able to do many calculations. However when one manages to fix the correct parameter values a number of interesting questions could be addressed. First of all one could try to verify the golden rule as presented by Schapotschinkow and Vlught in Ref. [13] for particles with a gold core. They performed simulations of the interactions between two capped gold cores in vacuum and concluded that for the position of the minimum in the interaction $r_{\text{min}}$ should always yield $r_{\text{min}} = 1.25d_c$, with $d_c$ the diameter of the core. This result is independent of the length of the polymers used to cap the spheres and is therefore very surprising. It is an open question to verify if the same holds for semiconductor clusters. We saw that for the parameter values used in the left part of figure 5.3, we obtained $r_{\text{min}} = 23\text{Å}$, i.e. $r_{\text{min}} = 1.15d_c$. So this seems to indicate that the golden rule is not valid for semiconductor nanoclusters. It is also interesting to investigate if another result from the same authors is valid for semiconductors. This result suggests that the capped gold spheres they use might form lines as the energy of 3 clusters in the linear configuration is lower than that in the triangle configuration. However before we can repeat this calculation for semiconductors using the model above, we have to solve another problem besides the fixing of the parameters. This problem consists of the steric interactions between three spheres. I do not see how the Alexander-de-Gennes model can be extended to incorporate a third sphere as this originates from the interactions between 2 infinite plates. To approximate the steric interactions between the 3 spheres in triangle configuration, by just calculating the steric interaction between spheres 1 and 2, 2 and 3 and 1 and 3 separately, seems to me to underestimate the interaction. This would especially be the case when there is an area where the capping layers of all 3 spheres overlap. So we see that there are a number of interesting open questions that the model presented in this chapter could solve. However more work will be needed before these questions can be answered.
Chapter 6

Interactions in solvent

Here I will present a method to extend the CDM to calculate the interaction energy between two nanoclusters in a solvent. For clarity I will refer to the model in vacuum as used before as CDM. In the first three sections I will introduce 3 methods to calculate the effects of a solvent which do not require extra particles to be included in our system. I will refer to these models as CDMS-1, CDMS-2 and CDMS-3. Then in section 6.4 I will treat the solvent particles as dipoles in exactly the same way as the cluster particles and this model I will call CDMS. As this method greatly increases the number of particles in our system I will then see if it can be approximated by any of the models discussed in the first 3 sections. Finally I will investigate if it is possible to also include the permanent dipoles of water molecules into our system.

6.1 First attempt to introduce a solvent: CDMS-1

6.1.1 Motivation

Here I will outline the motivation behind the first model to incorporate a solvent into our system. In this model we will treat the solvent as a continuum completely characterized by its known dielectric constant. We know from equation 2.17, that in absence of an external electric field the Hamiltonian of the system without a solvent is given by

\[ H = \frac{p^2}{2m} + \frac{m\omega_0^2}{2}u^2 - \frac{e^2}{2\epsilon_0}u^T \tau u. \] (6.1)

We note that the first 2 terms denote the energy of 2N uncoupled particles, whereas the third term gives the interaction between particles (both in the same cluster and between different clusters). To motivate this model I start with the easiest case of 2 clusters both consisting of a single particle (a dipole) in a solvent. As we view our particles as point particles this means that we have two point dipoles in a continuous sea of solvent. If we label the particles A and B then \( E'_A = E_A/\epsilon_r \), where \( E_A \) is the field created by particle A in absence of the solvent, \( E'_A \) is the electric field created with the solvent taken into consideration and \( \epsilon_r \) is the relative permittivity of the solvent. As the same holds for the field created by particle B equation 6.1 will change to

\[ H = \frac{p^2}{2m} + \frac{m\omega_0^2}{2}u^2 - \frac{e^2}{2\epsilon_r\epsilon_0}u^T \tau u. \] (6.2)

Now the problem can be solved in exactly the same way we did without the solvent, but with \( \epsilon_0 \) replaced with \( \epsilon_r\epsilon_0 \).

We now increase the size of the clusters A and B, so that they both contain N particles. For simplicity of the discussion I will assume both particles to be spheres and N to be so large that not all the particles are on the outside of the sphere. Again as always we will view our clusters as clusters of point particles (although the point particles do have a minimum separation) and we now arrive at the major problem, i.e. we will
have to decide what is in between these point particles. The easiest, but least physical option, is to assume that there is solvent in this area. This is not physical as this would mean that the solvent actually enters the clusters, which does not happen for densely packed, nonporous particles. However if we use this description we still have a continuous sea of solvent with a number of point dipoles dropped into it and therefore we can still describe the system by equation 6.2.

A more physical description would be to remove the solvent in the areas where the clusters A and B are located. So we take the area in between the particles that make up cluster A to be a vacuum and only allow the solvent outside the cluster (and similarly for cluster B, obviously). So the point dipoles are contained in a vacuum sphere surrounded by solvent. This means that the interaction between 2 particles in cluster A does not change as a result of the introduction of the solvent, which is obviously good. However the interaction between a particle in cluster A and one in cluster B now becomes much more complicated. The field that the particle in cluster B feels as a result of the particle in cluster A now passes through two surfaces (one when it leaves the vacuum of cluster A and enters the solvent and one when it leaves the solvent and enters the vacuum of cluster B). As the field behaves differently in the solvent and the vacuum we will have to calculate this separately and match the fields on the surfaces. However I do not see a way to incorporate this calculation into our present method.

A solution could be to use an approximation. For the interaction between 2 particles inside cluster A we use that the field only passes through vacuum. However, for the interaction between a particle inside cluster A and a particle inside cluster B we assume that the field only passes through the solvent. Physically this can be seen as a limit for a large distance between the particles, i.e. the part the field ”travels” through the solvent is much more important than the part it travels through the cluster. This approximation has the advantage that the calculation needs only minor alterations as I will show now. We know from equation 2.18 that we can rewrite equation 6.1 in the form

\[ H = \frac{p^2}{2m} + \mathcal{U}^T \mathbf{\Omega} \mathcal{U}, \]  

where

\[ \mathbf{\Omega} = \frac{m\omega_0^2}{2} (\mathbf{I} - \alpha_0 T) = \frac{m\omega_0^2}{2} \begin{pmatrix} I - \alpha_0 T_1 & -\alpha_0 T_2 \\ -\alpha_0 T_2 & I - \alpha_0 T_1 \end{pmatrix} \]  

with \( T_1 \) denoting the intra cluster and \( T_2 \) the inter cluster interactions. If we now define \( T_1' \) and \( T_2' \) to be the intra and inter cluster interactions with a solvent present, we conclude from the discussion above that we should merely replace \( T_1 \) and \( T_2 \) in equation 6.4 by \( T_1' = T_1 \) and \( T_2' = T_2/\epsilon_r \) in order to account for the solvent.

### 6.1.2 Results

I examined a system consisting of 2 spherical fcc packed clusters made from a 135 silica particles at varying inter cluster distance for two different solvents. The results are shown in figure 6.1. We clearly see that the effect of the solvent is very large. Closer examination of the result shows that \( V_{\text{solvent}}(r) = V_{\text{vacuum}}(r)/\epsilon_r^2 \). I have not drawn this line in the plots as it is indistinguishable of the lines that are already drawn, with a relative difference smaller than 0.6% for the parameter regime studied. We therefore directly see that the effect of any solvent will be very large, as they all have \( \epsilon_r > 1 \). Intuitively I think that the effect of the solvent is unphysically large, especially for two nearly touching clusters. The reason behind this is that this method assumes a large separation such that it is a good approximation to assume that most of the interactions between the clusters take place in solvent. However for (nearly) touching clusters this does not hold. In the next section I will attempt to remedy this.
6.2 Refining the method: CDMS-2

6.2.1 Motivation

In order to remedy its alleged shortcomings at small cluster-cluster distances, I propose an alteration of the model here, which I will call CDMS-2. Before I introduce this however, I first want to give the motivation behind this model. I keep the 2 most important assumptions from CDMS-1, namely that the space can be divided into three regions, two spherical clusters A and B and a continuum solvent in between, completely characterized by its static permittivity. Any model build on these two assumptions should in my opinion now satisfy 3 important conditions: (1) the solvent does not change the interactions between dipoles within the same cluster, and as a result the one-cluster energy does not change. This condition is set as we exclude the solvent from entering in the space between the dipoles (as they are contained in regions A and B). Note that this condition will only hold when areas A and B are convex, but for now I will assume that they are. Furthermore it should be noted that I set this condition in order to keep the model as simple as possible. We know from Maxwell theory that the presence of a solvent can also affect the electric fields in a nearby vacuum. However as there is no clear method of introducing this effect into the existing model, I have neglected this. (2) when two cubic clusters of similar size are positioned such that two of their sides touch along the entire surface, the solvent does not change the interaction energy between the two clusters. This condition follows directly from the first condition as the two cubic clusters now form one large convex cluster, whose energy by condition 1 does not change when we add a solvent. (3) in the limit of $\epsilon_r \to 1$ CDMS-2 should reduce to CDM. We note that model CDMS-1 does satisfy condition 1 and 3 but fails to satisfy condition 2.

I now introduce the CDMS-2, which I will define in such a way that it satisfies all three conditions above. I start by assuming that CDMS-2 can be written in the same form as CDM, i.e. the Hamiltonian is of the form given in equations 6.3 and 6.4. From condition 1 it is clear that in CDMS-2 can be written in the same form as CDM, i.e. the Hamiltonian is of the form given in equations 6.3 and 6.4. From condition 1 it is clear that in CDMS-2 the matrix $T_1$ will have to be the same as in CDM. So we can only alter the matrix $T_2$. In CDM we know that the matrix $T_2$ is build up form matrices $T^{(2)}_{ij}$ which have the behavior

$$\alpha_0 T^{(2)}_{ij} \sim \frac{1}{\epsilon_0 \epsilon_r r_{ij}^3},$$

which in CDMS-1 is modified into

$$\alpha_0 T^{(2)}_{ij} \sim \frac{1}{\epsilon_0 \epsilon_r r_{ij}^3 r_{ij}^3},$$

However as became clear above this failed to satisfy condition 2. To solve this problem I decompose $r_{ij} = r_{ij}^v + r_{ij}^s$, where $r_{ij}^v$ and $r_{ij}^s$ are the part of $r_{ij}$ contained in the vacuum and the solvent, respectively. Now
we assume that the matrices $T^{(2)}_{ij}$ behave as

$$\alpha_0 T^{(2)}_{ij} \sim \frac{1}{\epsilon_0 (r^v_{ij} + \sqrt{r^s_{ij}})^3}. \quad (6.7)$$

I will now show that with this form for the $T^{(2)}_{ij}$ model CDMS-2 satisfies all 3 conditions. It is clear that it satisfies the first equation as $T_1$ is unchanged. When we have two touching cubic clusters of the same size, we see that $r^s_{ij} = 0$ for all $i$ and $j$ so the model reduces to CDM and condition 2 is satisfied. This is also shown in the result section below, where I calculated the interaction energy between cubes according to CDMS-2. As $r_{ij} = r^v_{ij} + r^s_{ij}$ the third condition is also satisfied. So we see that this model satisfies all conditions and so far this is the only model I can think of that does. I cannot prove that there are no other models and it is possible that one can construct a model that also satisfies all 3 conditions.

6.2.2 Results

The results from CDMS-2 are very different from CDMS-1 as we see in figure 6.2. Here I studied again the system of 2 spherical silica clusters of 135 particles. We note a couple of important differences with the results from CDMS-1. First of all we see that at close range the interaction is much stronger, exceeding $kT$ at contact compared to $10^{-3} - 10^{-2}kT$ within CDMS-1. Secondly we note that the interaction falls off much quicker when there is a solvent present and as a result the interaction with a solvent can no longer be approximated by a multiple of the interaction without a solvent. Furthermore we note that even when the 2 spheres are touching there is still a large effect due to the solvent, as the attractive well of $\sim 1kT$ differs largely from the $\sim 5kT$ in vacuum. Therefore I have also studied the interaction between 2 cubes, both consisting of a 125 silica particles. We expect for cubes, that, as a result of condition 2, when they are touching the interaction should not change when we introduce a solvent. The results are shown in figure 6.3. We clearly see that the solvent has no influence when the particles touch, as expected. Furthermore we again see that the interaction falls off much faster with a solvent present than without.

6.3 Following the pairwise sum method: CDMS-3

Here I will present another easy method to include a solvent into our system. This method is based on the relation between Hamaker constants in vacuum and solvent. From Ref. [10] we see that we can find the Hamaker constant in a solvent by replacing the polarizability $\alpha_0$ in equation 4.5 in vacuum by $\alpha_0^{(c)} - \alpha_0^{(s)}$. 

Figure 6.2: Interaction energy for a spherical cluster of 135 silica ($r_{core} = 10 \text{Å}$) particles according to CDMS-2. The blue line is without solvent, the red line is for methanol and the green line is for water.
where \( \alpha_0^{(c)} \) is the static polarizability of a cluster particle and \( \alpha_0^{(s)} \) is the static polarizability of a solvent particle. Now the idea is to do the same in the CDM. To do this I first move to the dimensionless parameter \( v_i = \frac{\alpha_0^{(i)}}{\alpha_0^{(i)}} \) for reasons that will become clear in the next section when we discuss the CDMS model. We define the CDMS-3 model as the standard CDM model but now with \( v_c \) replaced with \( v_c - v_s \) in the Hamiltonian. We note that for silica clusters we have \( v_c = 0.1154 \). Now we need to find a correct value for \( v_s \). Here I will use water as solvent. From Ref. [16] we know that \( a_0 = 3.107\,\text{Å} \) for water molecules, where the static polarizability of water is reported to vary in the regime \( 1.04\,\text{Å}^3 \leq \alpha_0 \leq 1.44\,\text{Å}^3 \) and hence \( 0.03467 \leq v_s \leq 0.048 \). Again I will look at the interaction between two silica spheres consisting of 135 particles and the result is shown in figure 6.4. We see that the effect of the solvent is again large. First we note that also when the spheres are touching the solvent influences the interaction. Secondly we note that the behavior in this model is almost the same as in the standard CDM model. For \( v_s = 0.03467 \) the CDMS-3 value is always between 48.1% and 49.4% of the CDM value. Similarly if \( v_s = 0.048 \) then the CDMS-3 value varies between 33.5% and 34.6% of the CDM value. Finally we note that as this is in essence just the CDM model with a new value for \( \alpha_0 \) we can approximate it by a pairwise sum with a Hamaker constant defined.
by this new $\alpha_0$ and the error will be similar to the error seen in section 4.3.

6.4 Treating the solvent as fluctuating dipoles: CDMS

6.4.1 Description of model

So far we have seen 3 methods to include a solvent into our model, which do not require extra particles to be added. Here I will give a more accurate description of the interaction of 2 silica clusters in water, but this will however greatly increase the particle number. I will then use this result to see if any of the 3 models described above are a good approximation. We start by noting that a water molecule consists of 2 kinds of dipoles. We have the induced fluctuating dipole which behaves similarly to the dipoles in the clusters and the permanent dipoles which have a permanent magnitude but can change their orientation. In this section I will only consider the effects of the induced dipoles, in the following part I will also try to take the permanent dipoles into consideration. As the induced dipoles in water have a characteristic frequency similar to that of the silica particles I now assume them for simplicity to be equal. As the size of the water molecules, $a_0 = 3.107\,\text{Å}$ [16], is very near to the size of silica molecules, $a_0 = 3.569\,\text{Å}$ [8], I also assume these to be equal for simplicity. Furthermore I assume the water molecules to be fixed on a grid. I initially tried to use a random placement of the water molecules, but the effect of the random placement turned out to be too large, so I had to abandon this method. I will work mostly with a simple cubic grid but will also briefly discuss the effects of an fcc grid. I will now work with cubic clusters as these will fit into the grid better and the type of cubic cluster will be the same as that of the grid the water molecules are on. I again divide out the atomic length scale, which means that the static polarizability of an atom is replaced with $v = \alpha_0/a_0^3$ and all distances from now on are in units $a_0$. For the sc grid the model is now as follows. We start with a box of $30 \times 7 \times 7$ water particles. In this box we place 2 cubic silica clusters, both consisting of 27 atoms. We place them in such a way that they are in the middle of the $y$ and $z$ plane and are placed in the $x$ plane in such a way that there are 6 layers of water particles between the clusters and the side of the box. The setup, where I only drew the silica particles, is shown in figure 6.5. This setup we use as the reference point of our calculation and we assume that the interaction energy between the clusters is 0. Now we move the second cluster towards the first cluster and calculate the difference in interaction energy. To do this we use the theory of CDM for 2 different particle species as described in section 2.4. We take steps of $1a_0$ in the separation between the 2 clusters in order to ensure that the total number of particles in the system does not change and continue this process until the 2 clusters touch. All there is left to do now is to fix the parameter values of the system. I use here the same values as in the previous section so $v_c = 0.1154$ and $v_s = 0.03467$ or $v_s = 0.048$. Now the model is complete and we can start the calculations.

6.4.2 Results

We first determine the eigenfrequencies of the system of $30 \times 7 \times 7$ particles, including 2 clusters of $3 \times 3 \times 3$ silica particles and the remaining $30 \times 7 \times 7 - 54$ water particles on a simple cubic lattice, and from this the interaction energy $V_w$ follows, where the index $v$ indicates that the solvent is water. Likewise we can also calculate the interaction if the two silica clusters in vacuum and this is denoted by $V_v$. In figure 6.6 I plotted the value of the interaction energy as well as that of $R = \frac{V_v}{V_w}$ for both values of $v_s$. We see here that the effect

![Figure 6.5: Setup of the two silica clusters in the box with water particles. For clarity only the silica particles are drawn.](image)
of adding water is both very large and unexpected. For small distances \( r \leq 7a_0 \) the interaction strength in water decreases with as much as a factor 3 for \( r = 3a_0 \) compared to the interaction in vacuum. For large distances \( r > 7a_0 \) however the interaction increases, with as much as a factor 10 for the largest distances, but we will see that these values are subject to large uncertainties. In order to estimate the uncertainties I looked at the effects of enlarging the box and these results are shown in figure 6.7. As these calculations are very time and memory intensive I only performed them for \( v_s = 0.048 \). We note that increasing the size of the box enhances the flat part on the left side of the graph. Therefore it seems that for an infinitely sized system the line will probably be constant. We note from figure 6.6 that for \( r = 8a_0 \) the interaction is of the order 0.01\( kT \), so the part of the curve, where it is not yet constant is not of very much interest to us. As mentioned before I have also investigated if the interaction changes for an fcc grid instead of an sc grid. Here I have investigated the interaction between 2 silica fcc cubes of 32 particles each surrounded by water on an fcc grid. Most of the setup mentioned above stayed the same, except for some minor changes. First of all we now have to make steps of \( \sqrt{2}a_0 \) in the separation between the cubes in order to keep the particle number constant. Secondly the box is now smaller as the particles are packed more dense and the total particle number is limited by computational capabilities. In figure 6.8 I present the ratio \( R = \frac{V_w}{V_v} \) for \( v_s = 0.048 \) (the results for \( v_s = 0.03467 \) are similar). We see again that the curve is flat for small \( r \). However now we do not see that this area becomes larger for bigger boxes. However as the boxes are now quite a lot smaller than before this could become better for larger boxes.

Figure 6.6: Left: Interaction energy between to cubic silica clusters of 27 atoms each according to CDMS. The color coding is blue for \( v_s = 0 \) (vacuum), red for \( v_s = 0.03467 \) and black for \( v_s = 0.048 \). Right: Fractional interaction energy \( R = \frac{V_w}{V_v} \) for the same systems.

Figure 6.7: Fractional interaction energy \( R = \frac{V_w}{V_v} \) for \( v_s = 0.048 \) for increasing box size. The red line is for a 30 \( \times \) 7 \( \times \) 7 box, the black line for a 43 \( \times \) 9 \( \times \) 9 box and the green line for a 50 \( \times \) 7 \( \times \) 7 box. The picture on the right is a close-up of the picture on the left.
6.4.3 Comparison to approximations CDMS-1-3

Here I will compare the results from the CDMS method with the approximations I made in the previous sections. We have seen that the CDMS calculation yields a potential that for small $r$ is approximately a constant fraction of the vacuum interaction potential. Furthermore as the flat part of the curve increases in length with increasing box size, we expect the entire curve to be flat for an infinite box. This directly rules out the applicability of CDMS-2, as we saw that in this model the fall-off is much faster than in vacuum. The other two models, CDMS-1 and CDMS-3, do reduce to a constant fraction of the vacuum interaction energy and therefore might work. However on first sight the CDMS-1 model seems to overestimate the effect of the solvent (water) by a huge amount. We recall from section 6.1 that $V_{CDMS-1}(r) = \frac{V_v(r)}{\epsilon^2}$, where $V_{CDMS-1}$ is the interaction energy in solvent according to CDMS-1. So we see that for water $R_{CDMS-1}(r) = \frac{V_{CDMS-1}(r)}{V_v(r)} = 1/6400$ and that this is much smaller than the $R_{CDMS} \approx 0.38$, which we obtain from figure 6.7. Therefore one might be tempted to rule out the CDMS-1 model. This conclusion would however be premature, because there is a flaw in our calculation of the CDMS-1 value. We use $\epsilon_r = 80$, however this relative permittivity is caused both by fluctuating and permanent dipoles of the water molecules, whereas in the CDMS calculation we only looked at the fluctuating dipoles. Therefore it makes sense to replace $\epsilon_r$ with $\epsilon_\infty$, which is the relative permittivity caused only by the fluctuating dipoles. We use the Clausius-Mossotti relation [16]:

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{4\pi}{3} v_s,$$

(6.8)

and if we use $v_s = 0.048$ we find that $\epsilon_\infty = 1.75$. So we see that only a very small part of the relative permittivity of water is caused by the fluctuating dipoles. Therefore this method might be useful after all and I will compare the CDMS-1 method with $\epsilon_\infty$ as well as the CDMS-3 method with the CDMS result. In figure 6.9 I plotted $R$ for CDMS-1 and CDMS-3. We note that both CDMS-1 and CDMS-3 agree reasonably with the CDMS. However we see that CDMS-3 agrees better than the CDMS-1 for all distances except at contact. Furthermore we note that for $r \leq 6a_0$ the difference between CDMS-3 and CDMS is less than 15%. However for $r > 6$ both approximations become much worse, although this might already be caused by the finite size of the box.

6.5 Including the permanent dipoles

In the previous section we only included the induced dipoles of the water molecules, but this is only half of the picture as we know that water molecules also have a permanent dipole. First I want to estimate the field strength of this dipole in order to see if it is strong enough to have any influence. We know from Ref.
Figure 6.9: Fractional interaction energy $R = \frac{V_{CDMS}}{V_{CDMS}}$ for a $50 \times 7 \times 7$ box and $v_s = 0.048$. The red line is for $i = 1$ and the blue line for $i = 3$.

[16] that the strength of the permanent dipole is $p = 1.85D$, where $D$ is short for the "Debye" unit of dipole strength. Note that I use $p$ and $P$ here to denote the dipole vector and strength and that this is different from the polarization, which was also denoted by $p$ and $P$ in chapters 2 and 3. Furthermore we know that the field at position $r$ of an electric dipole in the origin is given by [17]:

$$E = \frac{1}{4\pi\epsilon_0} \left( \frac{3(p \cdot \hat{r})\hat{r} - p}{r^3} \right). \tag{6.9}$$

So we find that the electric field along the polarization axis at the minimum separation $r = a_0$ is of the order $E = 3.7 \times 10^9 V/m$ which is large enough to influence the interaction energy according to the results in section 4.2. Now the idea is to attach to every induced water dipole a permanent dipole with strength $p = 1.85D$ and random orientation. We then treat the permanent dipoles as fixed as they move much slower then the induced dipoles. So we repeat the calculation of the previous section but now with an external electric field generated by the permanent dipoles, which will vary in space. So we see that at the position of the $i$th particle the electric field is given by

$$E_i = \frac{1}{4\pi\epsilon_0} \sum_{j=2N_v+1}^{N} \left( \frac{3(p_j \cdot \hat{r}_{ij})\hat{r}_{ij} - p_j}{r_{ij}^3} \right), \tag{6.10}$$

where it is understood that if $i > 2N_v$ the case $i = j$ is excluded from the sum. However here we encounter a problem. We notice that we sum over 3 space dimensions over a function decreasing with $r^{-3}$, so this will not converge for infinite $N$. However as we work with a finite box this value will remain finite. This does not solve all our problems as the value can still get large. I examined a box of 250 water particles without any silica clusters to investigate the size of the effect of the electric field. Here I found that for some particles $E \sim 4 \times 10^{11} V/m$ and as a result the difference in energy between different randomly placed polarizations of the permanent dipoles is of the order $10^4 kT$. As this is 3 orders of magnitude larger than the largest VdW interaction it seems difficult to incorporate this into our model without losing all other information. For sure we would need a very large number of iterations to take all random effects into account and even then it is doubtful if we can get a reasonable answer. I wonder strongly if the permanent dipoles in liquid water are really randomly oriented or that they line up more or less. Furthermore I suspect that the effect of the permanent dipoles might be less if they where randomly placed and not put on a grid as I did.

6.6 Discussion

We have studied three simple models to include a solvent into our theory (CDMS-1-3) and compared these with the CDMS method where we treated all the solvent particles as fluctuating dipoles. We found that
CDMS-3 agreed the best with the CDMS value, although the discrepancy was always more than 7%. The CDMS-1 model also agreed quite well, when we worked with $\epsilon_\infty$, but is usually a couple percent worse than the CDMS-3 model. The CDMS-2 model predicts a different behavior than observed in the CDMS and is therefore rejected. Furthermore we should point out that CDMS-1 has one big advantage over CDMS-3. If we know the interaction energy between 2 clusters in vacuum we can then obtain their interaction energy in any solvent directly from CDMS-1, we only need to divide the potential by $\epsilon_\infty^2$, whereas for the CDMS-3 value we will need to repeat the entire calculation for every solvent. Therefore I do not want to make a choice between CDMS-1 and CDMS-3 at this moment. In the previous section we saw that we cannot include the permanent dipoles of the water particles into the model with our present method. We calculated in section 6.4 that the fluctuating dipoles only cause a very small portion of the relative permittivity of water. Therefore I doubt if the CDMS model is a good description of water as solvent, as the permanent dipoles it ignores might have more influence than the fluctuating dipoles it includes. However if we have a solvent consisting of particles with almost no permanent dipole, like hexane or toluene, the model should hold. Finally I like to point out that all the results presented in this chapter are new as far as I can tell. The three models presented in the first 3 sections have not appeared in the literature that I am aware of. Although Donchev [10] has discussed placing the solvent on a grid he did not examine cluster interactions in a solvent as I did in section 6.4.
Chapter 7

Conclusion

After introducing the theory behind the CDM, we started by calculating enhancement factors of the static polarizability for different clusters in chapter 3. Originally we found that the enhancement factor $f$ for cubic clusters increases monotonically with increasing size to what appeared to be a limit. However this did not coincide with our calculation that for infinite size clusters it should return to $f = 1$. We then tried to approximate the cluster to reduce its degrees of freedom, but this did not work. We did find that hollow cubes behave very differently and can be an interesting research object in itself. Using the approach of Bas Kwaadgras, which utilizes symmetries in the cube, we where able to calculate $f$ for much larger clusters and observed a decrease in its value. However as the decrease is still small, it is not yet clear, how $f$ behaves for larger clusters and this is still an open question. Furthermore we studied the local enhancement factors of the cube and found that, in contrast to results for squares [7], they do not assume a bulk value for the clusters studied but vary throughout the cluster. We also studied the enhancement factors of spheres and found these to decrease for larger clusters and it seems that they will return smoothly to $f = 1$, when the cluster size goes to infinity. We also took a look at linear clusters, but where unable to find new results there.

In chapter 4 we studied the interactions between 2 nanoclusters in vacuum. We first looked at linear clusters and examined the dependance of the interaction energy on their orientation. We found a vary strong dependance here. We also studied the effects of an external electric field and found these to be negligible for physically achievable fields. We then compared the interaction energies obtained from CDM with those obtained from the pairwise sum method and found that the discrepancy is between 5%-20%, depending on the size of the cluster and the Hamaker constant used. We also studied chain formation for both single particles and cubic clusters and found in both cases no evidence to suggest chain formation. Similarly Bas Kwaadgras [11] has shown that spherical clusters also show no signs of chain formation. Lastly I showed an interesting phenomenon we observed when increasing the length of linear clusters, whilst keeping their minimal separation constant. We observed that, depending on the separation and orientation, there can be an optimal length for which the interaction energy is minimal.

The next chapter dealt with interactions between capped spheres. We started by calculating the steric interactions between two capped spheres using the Alexander-de Gennes model. We then showed that, depending on the choice of parameters, capping layers made out of polymers can prevent aggregation. Furthermore we saw that the golden rule, defined by Schapotschnikow and Vlught [13], did not hold in this case. However, due to the number of parameters involved and the lack of available data concerning their values, we were unable to obtain more results for the two particle interactions. We could not study chain formation in this case, as their is no clear method to extend the Alexander-de Gennes model to three or more capped spheres.

The last chapter discussed methods of introducing a solvent into the model of interactions. We started by introducing three models CDMS-1-3, which needed no extra particles to be added into the system. We then compared them with the interaction energy obtained from CDMS, where we treat every solvent molecule, fixed on a grid, as a fluctuating dipole. We found that CDMS-2 did not agree with the CDMS values and
was therefore rejected. Both CDMS-1 and CDMS-3 agreed reasonably well with the CDMS values, where CDMS-3 seemed to perform slightly better than CDMS-1. However, CDMS-1 has the advantage that it is faster to calculate. Finally, we also tried to add permanent dipoles to our solvent particles, but this attempt was unsuccessful. It remains an open problem to introduce them into the theory.
Bibliography


