Finite Element Analysis of Multi-Body Interactions in Membranes and Colloidal Systems

by

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A Thesis Submitted For the degree of Doctor of Philosophy
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March 2009
Abstract

Colloidal interactions namely hydrodynamic and electrical forces are of a significant practical importance to many industries. Electrostatic interactions are one of the major forces affecting the stability and behaviour of a colloidal system. Thus, studying these interactions and understanding their behaviour will have very useful implications in many areas. The aim of this study is to quantify electrostatic interactions in multi-body colloidal systems using numerical methods to solve the governing equations for electrical potential and surface charge distribution.

Finite Element Method combined with error estimation and mesh refinement has been used to provide a flexible numerical solution to the 2D non-linear Poisson-Boltzmann equation in order to obtain the potential distribution, which is used to calculate the free energy of interaction and the electrostatic force for surface potential and surface charge density boundary conditions; for different geometries and settings. The FEM has been used to provide solution to 3D geometries as well. The schemes provide quantifications of the electrostatic interactions which is expected to be very useful in many fields, and to fill some of the void in numerical software vicinity, regards solving the non-linear PBE. This will help to gain more understanding of the nature of multi-body interactions, which is yet to be fully understood.

The model has been applied to a number of different study cases, in particular, that of a charged sphere approaching a charged wall, two identical charged spheres, chain of charged spheres, and a chain of spheres inside a chain of rings for the 2D model. The problem of two charged spheres approaching a charged wall and an array of charged spheres have also been solved in the 3D model.
The finite element method has proved to be effective in quantifying multi-body electrostatic interactions in 2D geometries and more complex 3D geometries. The 3D code has been first validated by comparison with previous 2D code results where very good agreement were obtained, and then extended to solve 3D cases where no previous solution exists.
Acknowledgements

I would like to thank all the people who made this work possible. First, I would like to express my gratitude to my supervisor Professor Adel Sharif who has been unfailingly generous with his help, encouragement, advice and commentary, not only during the process of researching and writing this thesis, but in my adjustment to the place when I first came and later on. His research ideas are innovative and well structured in his mind and he has a way of making complex problems sound simple and reachable. He is an example to follow both academically and personally. I would also like to thank my co-supervisor Professor Ugur Tuzun for his comments and recommendations during our review meetings. He always made a time when I needed feedback whether in research or journal paper discussion and writing. I would like also to thank to my other co-supervisor Doctor Andrew Tate who made dealing with computer issues much less painful in this university. He was actually able to put up with the proofreading of this thesis from cover to cover. He did take one for the team! And thanks to all the staff in the chemical engineering department for their assistance and friendiness.

I would also like to show my appreciation to Abu Zaid and the family. They have taught me a lot about life and culture in this country and were a real family for me here.

Finally, I would like to thank my family to whom I owe so much; to my father, mother, brother and sisters; to them I owe a debt which is ongoing, and can never be repaid.

Without all these people, this work would not have been a reality. Thank you.
Table of Contents

Abstract ii
Acknowledgements iv
Table of Contents v
List of Figures x
Nomenclature xx
Abbreviations xxii

1. INTRODUCTION 1
   1.1. Structure and outline 6
   1.2. Aim and objectives 8

2. COLLOIDS AND ELECTRICAL PROPERTIES OF COLLOIDS 9
   2.1. General characteristics of colloids 9
       2.1.1. The importance of colloids 12
       2.1.2. Colloids and membrane systems 16
       2.1.3. Classification of colloids 17
       2.1.4. Formation of colloids 20
       2.1.5. Particle size and shape 22
       2.1.6. Stabilization of colloid suspensions 23
       2.1.7. Coagulation 25
   2.2. Interactions between colloidal particles 29
       2.2.1. Excluded volume repulsion 29
2.2.2. van der Waals forces 29
2.2.3. Entropic forces 30
2.2.4. Steric forces 30
2.2.5. Electrostatic interaction 31

2.3. Electrical Properties of Colloids 33
2.3.1. Electrophoresis 34
2.3.2. The electrical double layer 34
2.3.3. Gouy-Chapman electrical double layer model 40
2.3.4. Colloids in the DLVO theory frame 41
2.3.5. Zeta potential 42
2.3.6. The conductivity of colloids 44
2.3.7. The influence of electrolytes on the charge of colloids 44

3. ELECTROSTATIC INTERACTION AND POISSON-BOLTZMANN EQUATION 46
3.1. Introduction 46
3.2. Gauss’ law 47
3.3. Debye-Huckel theory and the Poisson-Boltzmann equation 47
   3.3.1. The Debye-Huckel model 48
   3.3.2. Gauss’ law and the Boltzmann distribution law 49
   3.3.3. The Debye-Huckel parameter 50
3.4. Limitations of the Poisson-Boltzmann equation 51

4. SOLUTIONS OF THE GOVERNING EQUATIONS OF ELECTROSTATIC INTERACTIONS 54
4.1. Introduction 54
4.2. Approximate approach to solve equations of electrostatic interactions 56
4.3. Numerical approach
  4.3.1. Monte Carlo method
  4.3.2. Finite difference method
  4.3.3. Finite element method

5. MATHEMATICAL MODELLING AND GOVERNING EQUATIONS

5.1. Introduction
5.2. Poisson-Boltzmann equation
5.3. Governing equations
5.4. Numerical solution of the normalized PBE
5.5. Finite element method implementation

6. TWO-DIMENSIONAL MODELS

6.1. Introduction
6.2. Electrostatic interactions between sphere and wall
  6.2.1. Problem Definition
  6.2.2. Results and Discussion
6.3. Electrostatic interactions between two spheres
  6.3.1. Problem Definition
  6.3.2. Results and Discussion
6.4. Electrostatic interactions of confined and unbounded chain of spheres
  6.4.1. Problem Definition
  6.4.2. Results and Discussion
6.5. Electrostatic interactions of a chain of spheres inside a chain of rings
6.5.1. Problem Definition  97
6.5.2. Results and Discussion  99

7. THREE-DIMENSIONAL MODELS  105

7.1. Introduction  105
7.2. Electrostatic interactions of an isolated charged sphere  106
  7.2.1. Problem Definition  106
  7.2.2. Results and Discussion  107
7.3. Electrostatic interactions of a sphere and a wall  111
  7.3.1. Problem Definition  111
  7.3.2. Results and Discussion  113
7.4. Electrostatic interactions of two spheres  117
  7.4.1. Problem Definition  117
  7.4.2. Results and Discussion  118
7.5. Electrostatic interactions of an array of spheres  122
  7.5.1. Problem Definition  122
  7.5.2. Results and Discussion  123
7.6. Electrostatic interactions of two spheres and a wall  128
  7.6.1. Problem Definition  128
  7.6.2. Results and Discussion  130

8. CONCLUSIONS AND FUTURE WORK  137

8.1. Conclusions  137
8.2. Future work  138

References  140
Appendices:

Appendix A: Boltzmann distribution 145
Appendix B: Additional figures for two spheres and a wall 147
Appendix C: Mesh figures and potential fields 150
Appendix D: Two spheres and a wall potential gradient 161
Appendix E: Program flow-chart 167
## List of Figures

<table>
<thead>
<tr>
<th>Figure No.</th>
<th>Figure Caption</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 2.1</td>
<td>Comparing (approximate) colloids dimensions [nanolytics manual, 2007]</td>
<td>10</td>
</tr>
<tr>
<td>Figure 2.2</td>
<td>Microscopic images of colloidal system [Symposium info, 2005; Colorado uni]</td>
<td>11</td>
</tr>
<tr>
<td>Figure 2.3</td>
<td>Colloidal particles that have formed a gel [Piotr Habdas, Emory uni]</td>
<td>13</td>
</tr>
<tr>
<td>Figure 2.4</td>
<td>Kaolinite colloids mainly [Colloid Mobilization and Transport in Saturated Porous Media, Colorado uni]</td>
<td>27</td>
</tr>
<tr>
<td>Figure 2.5</td>
<td>The Coulomb potential: The (green) bottom curve represents the interaction between some two particles of opposite charge; while the (red) top curve represents the interaction of particles of equal charge [Wasser Manual 2000–2003]</td>
<td>32</td>
</tr>
<tr>
<td>Figure 2.6</td>
<td>The negatively charged particle is surrounded by positive ionic atmosphere</td>
<td>35</td>
</tr>
<tr>
<td>Figure 2.7</td>
<td>The electrical double layer</td>
<td>36</td>
</tr>
<tr>
<td>Figure 2.8</td>
<td>The electric potential near an electrically charged wall/particle with the blue spheres representing positive ions, while the red ones represent the negative counterions</td>
<td>37</td>
</tr>
<tr>
<td>Figure 2.9</td>
<td>Influence of electrolyte concentration on electrostatic potential in relation to distance</td>
<td>39</td>
</tr>
<tr>
<td>Figure 2.10</td>
<td>Net Interaction Energies at low and high Zeta Potential [Romo</td>
<td></td>
</tr>
<tr>
<td>Figure 2.11: Simplified diagram of particle interaction at low and high Zeta Potential [Romo &amp; Pitts, 1998]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&amp; Pitts, 1998</td>
<td></td>
<td></td>
</tr>
<tr>
<td>43</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Chapter 4:

<table>
<thead>
<tr>
<th>Figure 4.1: A spherical particle in an ionic solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>58</td>
</tr>
</tbody>
</table>

### Chapter 5:

<table>
<thead>
<tr>
<th>Figure 5.1: AB, EF are Boundary inlet and outlet respectively; GH sphere surface; DE pore surface; CD planar surface. AB and BC natural boundary; boundaries AH and GF, z axis, line of symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>72</td>
</tr>
<tr>
<td>Figure 5.2: Nine-node quadrilateral element</td>
</tr>
<tr>
<td>78</td>
</tr>
<tr>
<td>Figure 5.3: Twenty-seven-noded 3D element</td>
</tr>
<tr>
<td>80</td>
</tr>
</tbody>
</table>

### Chapter 6:

<table>
<thead>
<tr>
<th>Figure 6.1: Geometry and boundary conditions for the calculation of electrostatic effects on a sphere and a wall: CD the wall surface; EF sphere surface. AB and BC natural boundary; boundaries AF and ED, z axis, line of symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>82</td>
</tr>
<tr>
<td>Figure 6.2: Potential values from sphere surface to wall surface for surface potential of 1 on both</td>
</tr>
<tr>
<td>84</td>
</tr>
<tr>
<td>Figure 6.3: Potential values from sphere surface to wall surface for surface potential of 2 on both</td>
</tr>
<tr>
<td>84</td>
</tr>
<tr>
<td>Figure 6.4: Coarse mesh for the case of a charged spherical particle near a charged wall indicated by the right edge</td>
</tr>
<tr>
<td>86</td>
</tr>
<tr>
<td>Figure 6.5: Successively refined mesh for the case of a charged spherical particle near a charged wall indicated by the right edge</td>
</tr>
<tr>
<td>86</td>
</tr>
<tr>
<td>Figure 6.6:</td>
</tr>
<tr>
<td>Figure 6.7:</td>
</tr>
<tr>
<td>Figure 6.8:</td>
</tr>
<tr>
<td>Figure 6.9:</td>
</tr>
<tr>
<td>Figure 6.10:</td>
</tr>
<tr>
<td>Figure 6.11:</td>
</tr>
<tr>
<td>Figure 6.12:</td>
</tr>
<tr>
<td>Figure 6.13:</td>
</tr>
<tr>
<td>Figure 6.14:</td>
</tr>
<tr>
<td>Figure 6.15:</td>
</tr>
<tr>
<td>Figure 6.16:</td>
</tr>
<tr>
<td>Figure 6.17:</td>
</tr>
<tr>
<td>Figure 6.18:</td>
</tr>
<tr>
<td>Figure 6.19:</td>
</tr>
<tr>
<td>Figure 6.20:</td>
</tr>
</tbody>
</table>

**Chapter 7:**

<p>| Figure 7.1: | Solution domain of an isolated charged spherical particle: I sphere surface (half sphere); DABC, HEFG, DAEH, GFBC and DHGC natural boundary planes; AEFB symmetry plane boundary |
| Figure 7.2: | Comparing results for different values of reduced sphere radius against the dimensionless total free energy |
| Figure 7.3: | Comparing results for different values of reduced sphere... |
| Figure 7.4: | Electric potential at different distance values to spheres surface (Sphere potential = 1) |
| Figure 7.5: | Electric potential at different distance values to spheres surface (Sphere potential = 2) |
| Figure 7.6: | Electric potential at different distance values to spheres surface (Sphere potential = 3) |
| Figure 7.7a: | Solution domain of a spherical particle approaching a wall: I sphere surface (half sphere); GFBC wall surface; DABC, HEFG, DAEH and DHGC natural boundary planes; AEFB symmetry plane boundary |
| Figure 7.7b: | Cross section of the solution domain of a spherical particle approaching a wall: I sphere circle; BF represents wall plane, AB, FE, EA represents the natural boundary planes |
| Figure 7.8: | Potential values from sphere surface to wall surface for surface potential of 1 on both |
| Figure 7.9: | Potential values from sphere surface to wall surface for surface potential of 2 on both |
| Figure 7.10: | 3d mesh example for the case of a spherical particle approaching a wall with sphere-wall separation value of 2 |
| Figure 7.11: | The potential distribution for the case of a sphere near a charged wall for $\Psi_w=1$, $\Psi_s=1$ and $\kappa a=1$ case, with $L=2$ |
| Figure 7.12a: | Solution domain of two interacting identical spherical particles: I sphere surface (half sphere); DABC midplane of symmetry. HEFG, DAEH, GFBC and DHGC natural boundary planes; AEFB symmetry plane boundary |
| Figure 7.12b: | Cross section of the solution domain of two interacting identical spherical particles: I sphere circle; AB represents |
| Figure 7.13: | Comparing present results with those of the 2d model in terms of dimensionless electrostatic force between two identical charged spheres (reduced surface potential=1, reduced sphere radius=1) |
| Figure 7.14: | Comparing present results with those of 2d model in terms of dimensionless free energy of interaction for two identical charged spheres (reduced surface potential=1, reduced sphere radius=1) |
| Figure 7.15: | Comparing present results with those of the 2d model in terms of dimensionless electrostatic force between two identical charged spheres (reduced surface potential=2, reduced sphere radius=1) |
| Figure 7.16: | Comparing present results with those of 2d model in terms of dimensionless free energy of interaction for two identical charged spheres (reduced surface potential=2, reduced sphere radius=1) |
| Figure 7.17: | Solution domain of an isolated charged spherical particle: I sphere surface (half sphere); ABCD, EFGH, ADHE, BCGF and CDHG are midplanes of symmetry; ABFE symmetry plane boundary |
| Figure 7.18: | Comparison of results with different systems (reduced surface potential=1, reduced sphere radius=1) |
| Figure 7.19: | Comparison of results with different systems (reduced surface potential=2 reduced sphere radius=1) |
| Figure 7.20: | Electrostatic force results between array of spheres for dimensionless radius values 0.1, 0.5 and 1.0 (reduced surface |
| Figure 7.21: | Electrostatic force results between array of spheres for dimensionless radius values 0.1, 0.5 and 1.0 (reduced surface potential=2) | 126 |
| Figure 7.22a: | Solution domain of two interacting identical spherical particles: I sphere surface (half sphere); DABC midplane of symmetry; GFBC wall surface. HEFG, DAEH and DHGC natural boundary planes; AEFB symmetry plane boundary | 129 |
| Figure 7.22b: | Cross section of the solution domain of a spherical particle approaching a wall: I sphere circle; AB represents midplane of symmetry, BF represents wall plane, FE, EA represents the natural boundary planes | 129 |
| Figure 7.23: | Dimensionless electric force between two charged spheres near a charged wall with respect to separation distance between them (reduced sphere potential=1, reduced wall potential=1) | 131 |
| Figure 7.24: | Dimensionless electric force between two charged spheres near a charged wall with respect to separation distance between them (reduced sphere potential=1, reduced wall potential=3) | 131 |
| Figure 7.25: | Dimensionless electric force between two charged spheres near a charged wall with respect to separation distance between them (reduced sphere potential=1, reduced wall potential=5) | 132 |
| Figure 7.26: | Dimensionless electric force between two charged spheres near a charged wall with respect to separation distance between them (reduced sphere potential=2, reduced wall potential=2) | 133 |
| Figure 7.27: | Dimensionless electric force between two charged spheres near a charged wall with respect to separation distance between them (reduced sphere potential=2, reduced wall potential=4) | 133 |
| Figure 7.28: | Dimensionless electric force between two charged spheres near | |</p>
<table>
<thead>
<tr>
<th>Figure 7.29:</th>
<th>A charged wall with respect to separation distance between them (reduced sphere potential=2, reduced wall potential=6)</th>
<th>134</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 7.30:</td>
<td>The potential distribution for the case of two charged spheres approaching a charged wall for $\Psi_w = 5, \Psi_s = 1$ and $ka = 1$, with $Ds = 1, Dw = 2.0$ (repulsive behaviour)</td>
<td>136</td>
</tr>
</tbody>
</table>

**Appendices:**

<p>| Figure A2.1:          | Dimensionless electric force between two charged spheres near a charged wall with respect to separation distance between them (reduced sphere potential=1.5, reduced wall potential=3) | 148 |
| Figure A2.2:          | Dimensionless electric force between two charged spheres near a charged wall with respect to separation distance between them (reduced sphere potential=1.5, reduced wall potential=5) | 149 |
| Figure A2.3:          | Dimensionless electric force between two charged spheres near a charged wall with respect to separation distance between them (reduced sphere potential=1.5, reduced wall potential=3) | 149 |
| Figure A2.4:          | Dimensionless electric force between two charged spheres near a charged wall with respect to separation distance between them (reduced sphere potential=1.5, reduced wall potential=5) | 150 |
| Figure A3.1:          | Coarse mesh for the case of two charged spherical particles | 151 |
| Figure A3.2:          | Adaptive refined mesh for the case of two charged spherical |
| Figure A3.3: | The potential distribution for the case of two charged spheres with $\Psi_s=1$ and $\kappa a=1$ case, with $L=0.5$ | 152 |
| Figure A3.4: | Coarse mesh for the case of chain of spheres inside a tube | 153 |
| Figure A3.5: | Adaptive refined mesh for the case of chain of spheres inside a tube | 154 |
| Figure A3.6: | The potential distribution for the case of chain of spheres inside a tube with $\Psi_w=1$, $\Psi_s=1$ and $\kappa a=1$ case, with $L=0.5$ | 155 |
| Figure A3.7: | Coarse mesh for chain of spheres inside chain of rings case | 155 |
| Figure A3.8: | Adaptive refined mesh for the case of chain of spheres inside chain of rings | 156 |
| Figure A3.9: | The potential distribution for the case of chain of spheres inside chain of rings with $\Psi_w=1$ and $\kappa a=1$ case, with $L=0.5$ | 156 |
| Figure A3.10: | Coarse mesh for the case of alternative chain of spheres inside chain of rings system | 157 |
| Figure A3.11: | Adaptive refined mesh for the case of alternative chain of spheres inside chain of rings system | 158 |
| Figure A3.12: | The potential distribution for the case of alternative chain of spheres inside chain of rings system with $\Psi_s=1$ and $\kappa a=1$ case, with $L=0.5$ | 158 |
| Figure A3.13: | The potential distribution for the case of two charged spheres with $\Psi_s=1$ and $\kappa a=1$ case, with $L=1$ | 159 |
| Figure A3.14: | The potential distribution for the case of an array of spheres with $\Psi_s=1$ and $\kappa a=1$ case, with $L=1$ | 160 |
| Figure A3.15: | The potential distribution for the case of two spheres approaching a wall with $\Psi_w=1$, $\Psi_s=1$ and $\kappa a=1$ case, with $L_{\text{spheres}}=1$ and $L_{\text{sphere-wall}}=1.5$ | 161 |</p>
<table>
<thead>
<tr>
<th>Figure A4.1:</th>
<th>The potential distribution for the case of two charged spheres approaching a charged wall for $\Psi_w = 5, \Psi_s = 1$ and $\kappa a = 1$, with $D_s = 1, D_w = 2.0$ (repulsive behaviour)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure A4.2:</td>
<td>The potential gradient vector field for the repulsion case, where the right end represents the midplane</td>
</tr>
<tr>
<td>Figure A4.3:</td>
<td>The potential gradient in x-axis direction for the repulsion case, where the right edge represents the midplane</td>
</tr>
<tr>
<td>Figure A4.4:</td>
<td>The potential distribution for the case of two charged spheres approaching a charged wall for $\Psi_w = 5, \Psi_s = 1$ and $\kappa a = 1$, with $D_s = 1, D_w = 0.2$ (attractive behaviour)</td>
</tr>
<tr>
<td>Figure A4.5:</td>
<td>The potential gradient vector field for the attraction case, where the top and the right ends represent the wall and midplane respectively</td>
</tr>
<tr>
<td>Figure A4.6:</td>
<td>The potential gradient in x-axis direction for the attraction case, where the top and the right ends represent the wall and midplane respectively</td>
</tr>
<tr>
<td>Figure A5.1:</td>
<td>The program general flow-chart</td>
</tr>
</tbody>
</table>

161
162
163
164
165
166
167
**Nomenclature**

\( c_i \)  
Local concentration of ions of species \( i \) in bulk solution (kmol m\(^{-3}\))

\( c_i^0 \)  
Concentration of ions far from the particle concerned (kmol m\(^{-3}\))

\( C_i \)  
Relative concentration of ion species \( i \) \( \left( \frac{n_i}{\overline{n}} \right) \)

\( e \)  
Electronic charge (1.602x10\(^{-19}\)C)

\( F^* \)  
Dimensionless electrostatic repulsive force

\( F \)  
Dimensional repulsive force (N)

\( G \)  
Total free energy around a colloidal particle (J)

\( G^* \)  
Dimensionless free energy

\( I \)  
Ionic strength of the electrolyte, kmol m\(^{-3}\)

\( k_B \)  
Boltzmann constant (1.381x10\(^{-23}\) J K\(^{-1}\))

\( d \)  
Surface-surface separation distance (m)

\( D \)  
Dimensionless separation \( (D = \kappa d) \)

\( N_A \)  
Avogadro’s number (6.022x10\(^{23}\) mol\(^{-1}\))

\( n_i \)  
Mean number per unit volume of ions in the double layer (m\(^{-3}\))

\( n_i(\infty) \)  
Mean number per unit volume of ions in the bulk fluid (m\(^{-3}\))

\( r \)  
Radial co-ordinate (m)

\( R \)  
Dimensionless co-ordinates \( (R = \kappa r) \)

\( z \)  
Axial coordinate (m)

\( Z \)  
Dimensionless coordinates \( (Z = \kappa z) \)

\( x \)  
Axial coordinate (m)

\( X \)  
Dimensionless coordinates \( (X = \kappa x) \)

\( y \)  
Axial coordinate (m)

\( Y \)  
Dimensionless coordinates \( (Y = \kappa y) \)
$T$ Absolute temperature (K) 

$\lambda$ Sphere-radius/pore-radius 

$z_i$ Charge number of ion species $i$ 

$\kappa$ Debye parameter ($m^{-1}$) 

$\varepsilon$ Permittivity of the electrolyte ($= \varepsilon_0 \varepsilon_r$ F m$^{-1}$), where $\varepsilon_0$ is the vacuum permittivity ($8.854 \times 10^{-12}$ F m$^{-1}$), and $\varepsilon_r$ is the relative permittivity. 

$\psi$ Electric potential (V) 

$\Psi$ Reduced potential $\left( \psi = \frac{e \psi}{k_B T} \right)$ 

$\Psi_s$ Reduced potential at sphere surface 

$\Psi_w$ Reduced potential at wall planar surface 

$\Psi_{\text{tube}}$ Reduced potential at tube surface 

$\rho$ Volume charge density (C m$^{-3}$) 

$w$ Energy expended on moving the ion from infinite to the EDL (J) 

$\sigma_\psi$ Dimensional space charge density (C m$^{-3}$) 

$\sigma$ Non-dimensional space charge density 

$\sigma_s$ Reduced surface charge density at sphere surface ($\sigma_s = \partial \Psi_s / \partial N$)
## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D</td>
<td>Two Dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>Three Dimensional</td>
</tr>
<tr>
<td>AFE</td>
<td>Adaptive Finite Element</td>
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<tr>
<td>AFEM</td>
<td>Adaptive Finite Element Method</td>
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<tr>
<td>DL</td>
<td>Double Layer</td>
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<tr>
<td>EDL</td>
<td>Electrical Double Layer</td>
</tr>
<tr>
<td>EI</td>
<td>Electrostatic Interactions</td>
</tr>
<tr>
<td>FDM</td>
<td>Finite Different Method</td>
</tr>
<tr>
<td>FEM</td>
<td>Finite Element Method</td>
</tr>
<tr>
<td>LPBE</td>
<td>Linear Poisson-Boltzmann Equation</td>
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<tr>
<td>MB</td>
<td>Multi-Body</td>
</tr>
<tr>
<td>MC</td>
<td>Monte Carlo</td>
</tr>
<tr>
<td>MD</td>
<td>Multi-Dimension</td>
</tr>
<tr>
<td>NPBE</td>
<td>Non-linear Poisson-Boltzmann Equation</td>
</tr>
<tr>
<td>PB</td>
<td>Poisson-Boltzmann</td>
</tr>
<tr>
<td>PBE</td>
<td>Poisson-Boltzmann Equation</td>
</tr>
<tr>
<td>ZP</td>
<td>Zeta Potential</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

The word “colloid” was first introduced by Thomas Graham in 1861 - it originated from the Greek word “kolla” which means glue, he used this term to stress his view to what a colloid is; that he sees colloids as glue in a way. Graham's definition of the range of particle sizes that characterize the colloidal domain is still widely used today. Systems of this type, colloids, have special characteristics which are of great practical importance in many fields and industries, like membrane separation, powder technology, biochemistry and others.

Membrane separation technology is increasingly being utilized in chemical industry for a wide variety of applications such as removing water from organics using hydrophilic membranes. Major industrial applications are driving the membrane market and represent opportunities for membrane separation technologies to isolate a pure product or to produce higher level of purification of a given product.

Key end-use markets for membrane industry include water and wastewater treatment, food and drinks processing, pharmaceutical and medical applications, chemical processing and gas separations. The water and wastewater treatment market made up 54 percent of membrane demand in 2003. However, the pharmaceutical and medical market will post stronger gains through 2008, benefiting from solid growth in pharmaceutical shipments and the rising
importance of biotechnology, a segment requiring precise separations. Major advances are expected for membranes used in fuel cell applications, albeit from a small base [Freedonia Grp., 2004].

The growth will be most rapid for the ultrafiltration membranes, which are used in a wide variety of applications as the primary separation step and as a pre-treatment step for higher level separations technologies. Gains are also projected to be strong for reverse osmosis membranes (which is expected to grow by nearly 10 percent annually), which have the smallest pores and thus achieve a high level of purification. Microfiltration membranes, which accounted for the largest share of total demand in 2003, represent a better established and more mature segment of the market, benefiting from their wide use as a pre-treatment membrane. Other types of separation processes that incorporate membranes include pervaporation, nanofiltration, dialysis, electrodialysis and gas separations [Business Wire, 2004].

Technologies of membrane filtration are also finding use in genomics, proteomics, drug discovery, and general laboratory applications in life sciences research, while medical and bioscience research are generating demand for sophisticated membrane separation and ultra pure water.

In these processes particles separated can accumulate on the surface of the membrane. The control of formation of this covering layer is the main problem facing all membrane processes. In order to prevent complete blockage of the flow of filtrate, the membrane modules must be rinsed periodically. Other techniques may be used depending on the application and the situation. This can place a large economic restriction on membrane systems operation; it can lead to reduced performance, higher energy consumption, and eventually, failure to meet the regulatory standards by the deterioration of the product stream [Romo & Pitts, 1998].
Membrane fouling is a multifaceted phenomenon and typically results from several causes. The central part of the problem is interactions between fouling materials and membrane, and between fouling materials themselves. It has been recognized that electrostatic interaction and hydrophobic/hydrophilic interaction between membranes and fouling materials have a significant bearing on membrane fouling. This is particularly true of more difficult fouling problems caused by adsorption of natural organic matters and biopolymers on the membrane. Electrostatic interactions take place among functional groups of membranes, fouling materials, and water primarily through dissociation and polarization, which strongly depend on the pH, ionic strength, and concentrations of divalent and multivalent cations in the solution. Hydrophobic/hydrophilic interactions are functions of arrangement similarities between membranes and fouling materials, the types and density of functional groups on both membrane surfaces and fouling materials, and the solubility of molecules of fouling materials. The balance between the forces of electrostatic repulsion and hydrophobic adhesion determines the outcomes of membrane fouling, as well as the effectiveness of chemical cleaning [Liu et al., 1999].

Thus, it is important to choose the membrane that suits the precise purpose it is intended for - to increase the efficiency of the process. Controlling this process is not merely related to the membrane separate material size alone. Electrostatic interactions between the membrane and the solutes to be separated can be extremely important for these processes. Furthermore, it’s possible to control the importance of such interactions through careful selection of processing conditions, in particular pH, ionic strength and operation pressure [Bowen and Sharif, 1997].

Electromagnetic forces uphold the structure and drive the processes of the chemistry around us and inside us. Because of the long-range character of
Coulombic interactions, electrostatics plays a particularly important part in intra- and inter-molecular interactions of chemistry and biochemistry.

The interactions between colloidal particles control the operation of many important industrial processes and also determine the properties of the final products. For instance, electrostatics plays a vital role in determining the specificity, rate, and strength of interactions in a variety of biomolecular processes. Knowing the electrostatic potential, one can calculate the force of particle-particle interaction. Features of interparticle interaction are of great importance for the stability of colloidal dispersions. Common examples include clay minerals, paints, inks and detergents, in which repulsive electrostatic interactions between particles promote stability against coagulation induced by van der Waals’ attractive forces. The importance of electrostatic interactions is well established in the computational biology community; what is less clear, however, is how to compute these interactions.

Accurate modelling of the contributions of solvent, counter ions, and particle charges to the electrostatic field can often be difficult and typically acts as the rate-limiting step for a variety of numerical simulations. Rather than explicitly treating the solvent and counter-ion effects in atomic detail, continuum methods such as those based on the Poisson–Boltzmann equation (PBE) are often used to represent the effects of solvation on the electrostatic properties of a biomolecule. Despite this simplification, current methods for the calculation of electrostatic properties from the PBE still require significant computational effort.

The main problem under consideration in this study is that of describing the electrostatic interactions (EI) between solutes (dissolved ions) and membranes/particles and the parameters affecting these interactions and their behaviour in different conditions, and to provide models that are more
representative of real systems with more complex geometries than what's currently available, particularly for the behaviour of multi body interaction in concentrated systems.

The methodology through which EI are quantified, is solving the non-linear Poisson Boltzmann equation using adaptive Finite Element methods (FE), the PBE is the fundamental differential equation describing the distribution of electrical potential at charged surfaces in electrolyte solutions. The electrical potential will then be used to calculate the free energy of interaction of approaching electrical double layers and the resulting electrostatic force.

There are three components of the solvated system that we must consider in order to accurately model the electrostatic potential: the solute molecule, the solvent, and the solvated ions. The solute molecule is modelled as a dielectric continuum of low polarizability embedded in a dielectric medium of high polarizability which represents the solvent. The solvated ions surrounding the molecule are also modelled as a continuum, distributed according to a Boltzmann distribution. Combining Poisson's equation, which is used to describe the electrostatic behaviour of the point charges in the dielectric continuum, with the Boltzmann charge distribution for the solvated ions gives the nonlinear Poisson–Boltzmann equation (NPBE).

The Poisson-Boltzmann equation is the basis of our understanding of many phenomenon involving electrolyte solutions, electrode processes, colloid interaction, membrane transport, nerve conduction, transistor behaviour, and even plasma physics.
1.1 Structure and Outline

An overview of the rest of the thesis is now presented: Part I (Chapters 2 and 3), serves as the theoretical part for this study, where the background of this study is presented.

Chapter 2 begins with introducing the concept of colloids, and discusses the importance of colloids and colloidal systems in various fields and applications. Different classification systems for colloids are presented with brief descriptions for each system. Overview of the formation of colloids and the main methods involved in that are included, with brief discussion of colloidal particle size and shape after that. This is followed by a general overview on stabilization of colloidal systems and coagulation of such systems. In the following section, the different forces with an important role in the interaction of colloid particles are presented. Next section will discuss some important electrical properties and phenomenon of colloids and colloidal systems, such as the electrical double layer and the influence of charge on colloids.

Chapter 3 focuses on the discussion of the Poisson-Boltzmann equation, which arises in the Debye-Huckel theory of macromolecule electrostatics. The unknown function $\Psi(r)$ in the equation represents the electrostatic potential generated by a macromolecule lying in an ionic solvent. Since the fundamental forces in molecular systems are electrostatic in origin, calculation of the potential using Poisson-Boltzmann equation is useful for several applications in biophysics, and in particular the electrostatic forces needed for molecular and Brownian dynamics simulation can be computed from the potential. Some of the properties of the Poisson-Boltzmann equation that make it a difficult problem for both analytical and numerical techniques are then mentioned.
Part II (Chapters 4 and 5) discusses the different methods used for solving the Poisson-Boltzmann equation, and then presents the solution model used in this study.

In Chapter 4, the solution approaches used to solve of the governing equations of electrostatic interactions are presented. Discussion of some special case solutions is included. This is followed by sections on the major numerical approaches to deal with the electrostatic interactions.

Chapter 5 presents the mathematical formulation and governing equations that constitute the basis of the model used in the present study.

Part III (Chapters 6, 7 and 8) is devoted to the discussion and analysis of the various case studies.

Chapter 6 is devoted to discuss the two-dimensional models investigated in this study, where we have four cases; that of a sphere and a wall, two spheres, a chain of spheres and a chain of spheres inside a chain of rings. Each problem is first defined, and then followed by graphical presentation and discussion of the numerical results.

In Chapter 7, we present the three-dimensional models, where we have five cases; the case of a single charged sphere, a charged sphere and a charged wall, two charged spheres, an array of charged spheres and two charged spheres and a charged wall. Results are then discussed and compared favorably with previous work.

Chapter 8 presents final conclusions to both the two-dimensional models and the three-dimensional ones, followed by recommendations for future work.
1.2 Aims and Objectives

The main interest of this study is to quantify the effect of multi-body electrostatic interactions (EI) in membranes and colloidal systems. This requires solving the non-linear Poisson Boltzmann equation, which will be carried out using the Finite Element method and the results are expressed in terms of the free energy of interaction and electrostatic force.

The model has been applied in this study to various types of geometries and for different surface properties (potential and surface charge); particularly, for two dimensional cases: (i) of a charged single spherical particle and a charged wall; (ii) two interacting identical spherical particles; (iii) a chain of identical spherical particles; (iv) a chain of identical spheres inside a chain of rings; and for three dimensional cases: (i) of the case of single isolated sphere; (ii) of a charged single spherical particle and a charged wall; (iii) two interacting identical spherical particles; (iv) an array of charged spherical particles; (v) and the case of two charged spheres approaching a charged wall.

To test the 3D code, results in terms of electrostatic force and free energy of interaction are obtained for a case of two interacting identical spherical particles for which previous 2D numerical solutions are available to compare with [McCartney and Levine, 1969], and in terms of electrostatic force for the case of a chain of spheres with data from [Sharif et al., 2003]. The 3D code then used to obtain numerical solution of geometries where no previous solution is available including, for example, the case of two charged spheres approaching a charged wall. Calculations have been carried out for ranges of different values of sphere surface potential/sphere charge, sphere radius/tube radius ratio, sphere/wall potential.
Chapter 2

Colloids and Electrical Properties of Colloids

2.1 General Characteristics of Colloids

Colloids can be defined as substances consisting of a homogeneous medium and particles dispersed in that medium. Colloidal particles are smaller than coarse, filterable but larger than atoms and small molecules. Although there are no precise boundaries of size between the particles in mixtures, colloids, or solutions, colloidal particles are usually of the order of $10^{-9}$ to $10^{-7}$ m in size [Lexico, 2006]. Such particles are normally invisible even with a microscope; their presence can be confirmed with the use of an ultramicroscope or an electron microscope. Homogeneous mixtures with a dispersed phase in this size range may be called colloidal aerosols, colloidal emulsions, colloidal foams, colloidal dispersions, or hydrosols.

A hydrocolloid can be defined as a colloid system in which the colloid particles are dispersed in water. A hydrocolloid has colloid particles spread throughout the water and depending on the quantity of water accessible can take on different states, e.g., gel or sol (liquid). Hydrocolloids (as colloids) can be either irreversible (single-state) or reversible. For example, agar, a reversible hydrocolloid of seaweed extract, can exist in a gel and sol state, and alternate between states with the adding or removal of heat.
A lot of hydrocolloids are derived from natural sources. For instance, carrageenan is extracted from seaweed, gelatin has bovine (cow) and fish origins, and pectin is extracted from citrus peel and apple pomace. Hydrocolloids are used in food mainly to manipulate texture or viscosity (e.g., a sauce). Hydrocolloids are also used in skin-care and wound-dressing.
Fig. 2.2. Microscopic images of colloidal system [Symposium info, 2005; Colorado uni]

Nowadays colloid science is the study of systems concerning small particles of the order of $10^{-9}$ to $10^{-7}$ m in size some substance dispersed in another. Dispersions in liquids form the basis of a wide range of systems of scientific and technological significance, including paints, ceramics, cosmetics, agricultural sprays, detergents, soils, biological cells, and many food preparations. About every theoretical
procedure and technique of modern physics and chemistry has been and is being applied to the study of colloids.

2.1.1 The Importance of Colloids

A crucial part of any study of chemistry and physics involves first the recognition of three states of matter (solid, liquid, and gas) and a general discussion of the transformations (melting, sublimation and evaporation) between them.

Attention is given to pure substances and then passes to solutions, which are homogeneous mixtures of chemical species dispersed on a molecular level. What remained unrecognized for the most part until about a century and a half ago was that there is kind of an intermediate category of materials lying between bulk and molecularly dispersed systems, in which, although one component is finely dispersed in another, the extent of subdivision does not approach that in simple molecular mixtures.

Systems of this type, colloids, have special characteristics which are of great practical importance. They consist of a dispersed phase (or discontinuous phase) distributed uniformly in a finely divided condition in a dispersion medium (or continuous phase).

Examples of colloidal systems are [Synlube, 2005]:

- Paints, muds and slurries (dispersions of fine solid particles in a liquid medium = sols or colloidal suspensions).
- Fogs, mists and smokes (dispersions of fine liquid droplets or solid particles in a gas = aerosols)
- Jellies (dispersions of macromolecules in liquid = gels).
• Opal and ruby stained glass (they are dispersions of, respectively, solid silica particles in a solid matrix or of gold particles in glass = solid dispersions).

• So-called photographic emulsions are dispersions of finely divided silver halide crystallites in a gel (in a sense they are a colloid within a colloid as the gel can be classified as a colloid).

Most if not all of the early and modern craft industries draw much of their technical capability from colloid science. In paper-making both the cellulose fibre used as meshwork and the clay used as a filler to improve opacity and produce a shiny texture are examples of colloidal systems. The inks used in ball point pens, in xerography, and in high speed printing presses each owe their special properties to their colloidal character, as do also the many varieties of cosmetics and colouring processes.

Fig.2.3a. Colloidal particles that have formed a gel [Piotr Habdas, Emory uni]
Aside from the widely recognized colloidal nature of protein and polysaccharide solutions there are various other biological systems that have been studied by methods of colloid science. The flow properties of blood are best understood in terms of its being a colloidal dispersion of deformable flat plates of the red corpuscles in a liquid. The flow properties of faecal material at times must be manipulated by colloid chemical techniques to avoid unpleasant physiological consequences. The synovial fluids that lubricate the joints and bearing surfaces in the body owe their properties to their colloidal character. Also the adhesion between cells and the interaction among antigens and antibodies is currently being treated by the same mathematical theory that applies to the coagulation of colloidal particles. Large part of food processing, preserving, and packing industry depends greatly on colloid chemistry, and agricultural scientists require knowledge of the colloidal properties of soils in order to bring optimum plant growth. Recent colloidal microcapsule techniques allow controlled release of a drug and, in some cases, precise targeting onto a specific organ. Aqueous emulsions of perfluoro-hydrocarbons have recently been developed as (temporary) blood substitutes.
[Riess and Le Blanc 1978]. The specific adsorptive properties of colloids can also be used to eliminate, to concentrate and possibly to recover industrial products such as metal ions from air and water [Hunter, 2001].

Dispersions of small solid particles in a liquid are used to produce coatings (paints, inks, paper coatings), composite materials (reinforced elastomers) and ceramics. They can be found also in food (milk, cheese), pharmaceuticals, and biotechnology processes (fermentation broths). Lastly, they form the bulk of industrial and city effluents. In most cases, it is at some point needed to separate the particles from the liquid: ceramic pastes have to be consolidated, clays and sludge have to be dewatered, and paper coatings have to be drained and dried. At this point major technical problems occur.

The solid/liquid separation can be achieved through a variety of processes such as mechanical compression, drying, filtration, and centrifugation. In all of these processes, the particles are pre-aggregated to form a flocculated suspension, and the liquid phase that separates the aggregates is removed until the aggregates attach to each other and form a wet cake. Some stress is then applied to the cake to remove more of the liquid phase and attain an optimal solid/liquid separation. This stress is an osmotic pressure (it moves the liquid with respect to the particles), which is applied through the processes listed above. The efficiency of the separation relies on the way in which the wet cake responds to osmotic pressure [Madeline et al, 2007].

In some of the above examples, which may be called simple colloids, a clear distinction can be made between the disperse phase and the dispersion medium. However, this may not always be the case; in network colloids this is hardly possible since both phases consist of interpenetrating networks, the elements of each being of colloidal dimensions. Porous solids, in which gas and solid networks
interpenetrate, two-phase glasses (opal glasses) and many gels are examples of this category. Similar situations arise when oil and water co-exist in the pores of an oil-bearing rock, also in frost heaving when water and ice co-exist in a porous medium.

### 2.1.2 Colloids and membrane systems

One of the main problems in the operation of membrane process is membrane fouling. Membrane fouling can be defined as a decline in flux of a membrane filter caused by the accumulation of particular constituents in the feed water on the membrane surface or in the membrane matrix. Mineral, colloid and biofouling are the main subgroups of fouling. In biofouling, for example, there has to be an initial adhesion point of the microorganisms and colloidal particles onto the membrane surface for it to take place. Colloidal particles such as mineral and biological particles can be found in all untreated water sources [Stumm & Morgan, 1996].

The surface charge is very likely to influence initial microbial adhesion. Majority of bacteria are slightly negatively charged in aqueous systems. The electrolyte concentration, which also influences the electrostatic double layer, has been found to influence primary adhesion [Amjad, 1992]. It is at this part where biofouling should be controlled. By stopping bacteria and mineral deposits from forming or adhering onto the membrane surface, the initial stage of biofouling (which is a condition to the rest of the process) will be eliminated.

The fact that a lot of organic and mineral colloidal particles have a negative charge in aqueous environments causes them to repel one another, and thus maintaining the stability of dispersion [Kemmer, 1988]. This may be explained by the loss of H atom from the organic particles.
2.1.3 Classification of colloids

Colloidal particles can be classified into several groups:

1. *Organic and inorganic colloids:*

Depending on their chemical composition colloidal solutions (sols) are considered either organic or inorganic colloids. The organic colloids are classified as homopolar sols (rubber in benzene), hydroxyl sols (starch) and heteropolar sols (proteins) according to Hermann Staudinger (1881-1965). The sols of inorganic colloids can be further grouped into colloidal solutions of elements, oxides, hydroxides and salts.

2. *Molecular and miscellar colloids:*

Colloids can be classified into molecular and miscellar colloids. ‘Molecular’ colloid particles are single macromolecules, and their structure is the same as that of small molecules – the atoms are joined by true chemical bonds. These molecular colloids are ‘true colloids’. ‘Miscellar’ colloid structure is quite different. Their particles are not large molecules but may aggregates of many small molecules of groups of atoms, which are held together by secondary valences, e.g. van der Waals forces. A miscelle is usually less stable than a macromolecule.

3. *Globular (sphero-) and fibrous (linear) colloids:*

Another important factor in the classification of colloids is the particle shape. All colloids may be classified into sphero- and linear colloids. The sphero- colloids
have more or less compact, globular particles while the linear colloids possess long fibrous units.

4. *Solvation of Colloids:*

This is the oldest classification of colloids, and it takes into account the stability of sols, and thus we will devote more attention to it. Here, all colloids can be either lyophilic or lyophobic. The lyophobic colloids are less stable than the lyophilic ones. When the dispersion medium is water, the terms hydrophilic and hydrophobic are used.

Lyophilic means 'liking a liquid'. In lyophilic colloids there is interaction between solvent and the particles where the former is combined with the latter. Lyophobic means 'disliking or fearing the liquid'. In lyophobic sols there is no affinity between the solvent and the particles. The stability of these sols depends on the charges of the particles.

Kruyt (1952) uses the same classification to refer to them as reversible and irreversible systems, respectively. This terminology expresses more clearly the real nature of distinction because the definitive test of whether a system is lyophilic is to determine whether the dispersion process takes place spontaneously when the solvent is added to the colloid. As with most such dichotomies, additional studies have shown a complete range of intermediate types, but it is still useful to differentiate between the extremes.

One factor contributing to the difference in behaviour between reversible (lyophilic) and irreversible (lyophobic) systems is the degree to which the dispersion medium is able to interact with the atoms of the suspended particle. If the dispersion medium can have contact with all or most of those atoms then
salvation energy will be important and the colloid should be lyophilic (reversible) on some suitable solvent. If it is prevented, by the configuration of the suspended particles (i.e. the disperse phase) then the colloid will almost definitely be lyophobic (i.e. irreversible) in its behaviour, even if the surface atoms interact strongly with the solvent. An exception is the case of some microemulsions which appear to be reversible (that they form readily with a minimal mechanical energy input) even though the size of emulsion drops can be ~20 nm.

The lyophilic colloid solution is stable thermodynamically since there is a reduction in the Gibbs free energy (called 'available energy' at times) when the 'solute' is dispersed. The strong interaction between 'solute' and solvent normally supplies sufficient energy to break up the disperse phase and there is usually an increase in entropy as well; any reduction in solvent entropy because of the interaction with 'solute' is generally more than compensated by the entropy increase of the 'solute'. For lyophobic colloid, the Gibbs free energy increases when the disperse phase is distributed through the dispersion medium so that it is a minimum when the disperse phase continues in the form of a single lump. A lyophobic colloid can then only be dispersed if its surface is treated in some way that results in a strong repulsion between the particles. This way, the particles can be prevented from aggregating (or coagulation) for long periods, although it should be emphasized that they are still thermodynamically unstable and the barrier to coagulation is a kinetic one. Given enough time they will form an aggregate eventually [Hunter, 2001].

2.1.4 Formation of Colloids

There are two basic methods of forming a colloid: reduction of larger particles to colloidal size, and condensation of smaller particles (e.g., molecules) into colloidal
particles. Some substances (e.g., gelatin or glue) are easily dispersed (in the proper solvent) to form a colloid; this spontaneous dispersion is called peptization.

1. Dispersion methods:

In dispersion methods, a sample of the bulk material is broken down to colloidal size by some kind of mechanical process. The most direct method is grinding in a colloid mill; a mechanical device that subjects a suspension of coarse particles to a high shear field by forcing it into a thin gap between two surfaces that are rapidly rotating with respect to one another. The particles (e.g., paint pigment) are then shattered by the shearing process and a colloidal dispersion results, assuming that the solution contains an appropriate dispersion agent to prevent the small particles from aggregating together. A similar effect can be achieved, particularly with emulsions (liquid-in-liquid dispersions), by subjecting a mixture of the two phases to a high frequency sound wave (~20 kHz). This process also requires the presence of a dispersing agent to result in a stable sol.

Sols can also be created by passing an electric arc between two wires positioned under the surface of a liquid (known as Bredig’s procedure). This is also an example of a dispersion method in that some of the sol almost definitely results from pieces of metal being torn from the surface of the wire; there is, however, some condensation from the vapour involved [Hunter, 2001].

2. Condensation methods:

Condensation methods are more numerous and more diverse, and perhaps more important for fine material. Condensation of smaller particles to form a colloid generally involves chemical reactions - typically displacement, hydrolysis, or oxidation and reduction [The Columbia Encyclopedia, 2005], they may involve
dissolution and reprecipitation, condensation from the vapour or chemical reaction. Example of the first type is the formation of solid paraffin sol in water. This can be done by dissolving paraffin wax in ethanol and pouring a little into a large volume of boiling water. The ethanol rapidly boils off leaving an opalescent dispersion of the paraffin. One example of the second category is that of the spontaneous formation of mist or fog from a supersaturated vapour; assuming the level of supersaturation is sufficiently high, the formation of various droplets of very small size is guaranteed.

The chemical methods can involve oxidation, reduction or double decomposition. Metal sols can be formed using reduction. The particles are small usually (<100 mm) and can be well stabilized that they act as though they were lyophilic particles [Frens and Overbeek, 1969].

Various inorganic compounds that are insoluble in water can be manipulated to form colloidal dispersions if they are formed by mixing rather concentrated reagents, particularly when a dispersion agent is found. Hence, barium sulphate sols can be prepared by mixing (NH₄)₂SO₄ and Ba(SCN)₂ with a little potassium citrate to act as dispersant. Arsenious sulphide sols are prepared by bubbling H₂S through a solution of As₂O₃ while silver halide sols are prepared by mixing silver nitrate and alkali halide solutions. It is usually necessary in gravimetric analysis procedures to treat a precipitate (e.g. BaSO₄) in a particular way to prevent the formation of a colloidal sol or to aggregate a sol, once formed, to be able to filter it effectively.

There are other types of chemical reactions that are valuable in certain situations but of limited applicability. Photodecomposition is, for instance, important in preparing silver particles from AgBr in photographic processes. Hydrolysis is also an important technique to prepare transition metal oxides and hydroxides sols; it
has been well exploited by some in the preparation of highly monodisperse systems (i.e. systems of uniform particle size) [Hunter, 2001].

2.1.5 Particle size and shape

The most important characteristics of various colloidal dispersions (especially dispersions of solids in liquids and aerosols) are the size and shape of the particles, since most other characteristics of the system are influenced to some extent by these factors.

Most colloidal dispersions of scientific and technological interest have particles that differ noticeably in size and may be of irregular shape. In the process of studying such systems, they may be approximated as spheres, or occasionally as spheroids, cylinders or sometimes as infinite flat plates. Octahedral, rhomboidal or cubic crystals, more so if they are small, will often act like spheres, while long parallelepipeds can be approximated as cylindrical rods.

Direct microscopic observation has developed significantly since the inclusion of transmission electron microscope (TEM), and later the scanning electron microscope (SEM), such that we can now determine the shape of many colloidal particles with very little residual uncertainty.

There are also several indirect methods of estimating the size of particle in colloidal dispersions, of which the oldest and most widely used rely on the principles of sedimentation rate determining.

Other methods used to estimate particle size include that of the electrical pulse counter which depends on the theory of the Coulter counter, in addition to the
different light scattering methods. Another recent development in the sizing of (particulate) colloidal dispersions is the use of hydrodynamic chromatography (HDC).

Surface area measurements allow estimations to particle size, if one can make few assumptions about particle shape. Surface area is most readily measured by an adsorption process, which aims to find out the area occupied by the ‘adsorbate’ molecule, and then the area of the underlying surface (the adsorbent) can be determined.

**2.1.6 Stabilization of colloid suspensions**

Stabilization is the means to keep the colloids from settling on the ground of the container or gluing together (aggregating). Presently, there exist remarkably few methods by which colloid stability can be imparted in a controlled fashion. The primary reason for this is the difficulty of ensuring that the repulsion extends over the required distance of several nanometres.

Steric stabilization and electrostatic stabilization are the two main mechanisms for colloid stabilization. Electrostatic stabilization is based on the mutual repulsion of like electrical charges.

Different phases have different charge affinities in general, so that a charge double-layer forms at any interface. Small particle sizes lead to huge surface areas, and this effect is greatly amplified in colloids. In a stable colloid, a dispersed phase mass is so low that its buoyancy or kinetic energy is too little to overcome the electrostatic repulsion between charged layers of the dispersing phase. The dispersed particles charge can be observed by applying an electric field: all
particles drift to the same electrode and therefore all of them must have the same polarity.

In systems like lyophobic or irreversible colloidal systems, the free energy is lowest when the particles are all condensed into one large lump together. Such systems can stay as individual particles for a good time only if some mechanism prevents aggregation during a collision. There are two ways in which this can be done:

a) The particles can be given an electric charge (either positive or negative) and if all have the same charge they will repel one another more or less strongly when they approach.

b) The particles can be coated with an adsorbed layer of some material (say a polymer), which itself prevents their close approach.

Mechanism (a) is referred to as electrostatic stabilization and mechanism (b) as steric stabilization. A system is colloidally unstable if collisions result in the formation of aggregates. Such a process is called coagulation, or sometimes flocculation.

1. Electrostatic stabilization:

It has been recognized in lyophobic colloidal dispersions that some degree of coagulation is always taking place at microscopic level, even at very low electrolyte concentrations when the sol appear to be quite stable macroscopically. This is to be expected, as it is suggested that lyophobic sol is metastable thermodynamically with respect to aggregation and considered ‘stable’ only in a kinetic sense, i.e. the rate of coagulation can be very slow. In this setting the presence of a ‘stabilizer’ (electric charge) sets up a repulsion barrier between
approaching particles. This reduces the efficiency of collisions and makes it much less likely for collisions to result in a permanent particle-particle contact.

2. Steric stabilization:

Steric stabilization (or sometimes called polymeric stabilization) has been used by human for a long time, even though its mechanism of operation has only recently become available for study. The early makers of inks and paints were aware of the significance of some natural gums in promoting the stability of their pigments (in the colloidal sense, this phenomenon was referred to as ‘protection’.

Thus the surface of the lyophobic colloidal particle was covered with lyophilic material of a polymeric (or a long-chain in general) nature. When two of this type of particles approaches, the interaction between those adsorbed chains causes enough repulsion to induce stability. The magnitude of this repulsion can be calculated by estimating the particle separation distance effect on the free energy of the adsorbed molecules. As they are forced together the number contacts between the chains is increased at the expense of the chain-solvent interactions and that leads to an increase in free energy (or a repulsive force) for a lyophilic molecule [Hunter, 2001].

2.1.7 Coagulation

As mentioned before; in unstable colloidal dispersions, such as lyophobic sols, there’s always some degree of coagulation existing at microscopic level because of interparticle attractions. If this coagulation is allowed to go on long enough, the particle aggregates become large enough to be observable. They are then called ‘flocs’ and if they differ in density from the surrounding medium, as is usual for oil in water emulsions, the aggregate accumulates at the top [Hunter, 2001].
The destruction of a colloid (coagulation or sometimes called flocculation) can be accomplished by a number of different methods [Lexico Publishing Group's Reference, 2006]:

- Heating to increase the velocities of the particles, causing them to collide with enough energy to penetrate the barriers so particles can aggregate. Since this is repeated many times, the particle will grow to be large enough to form a precipitate.
- Eliminating the electrostatic barrier that prevents aggregation of the particles. This can be done by the addition of suitable salt to a suspension or altering the pH of a suspension to effectively neutralize or "screen" the surface charge of the particles in suspension. This removes repulsive forces that keep colloidal particles separated and allows for coagulation due to van der Waals attractive forces.
- Adding a charged polymer flocculant. Polymer flocculants can link individual colloidal particles by attractive electrostatic interactions. For instance, negatively-charged colloidal silica particles can be flocculated by the addition of a positively-charged polymer.
- Addition of non-adsorbed polymers known as depletants can cause aggregation due to entropic effects.
- Physical deformation of particles may increase the attractive van der Waals forces more than ‘stabilization’ forces (such as electrostatic), causing coagulation of colloids at certain orientations.

Unstable colloidal suspensions of low-volume fraction form clustered liquid suspensions, wherein individual clusters of particles drop to the bottom of the suspension (or float to the top if their density is less than the suspending medium) once the clusters are of sufficient size that gravitational forces overcome the Brownian forces that keep the particles in suspension. However, colloidal
suspensions of higher-volume fraction can form colloidal gels with viscoelastic properties. Viscoelastic colloidal gels flow like liquids under shear, but keep their shape when the shear is removed.

Addition of electrolyte as a coagulation agent may influence a phenomenon called Rapid coagulation. This happens when there is no electrical barrier to the particle approach and every collision results in contact.

The electrolyte concentration at which slow coagulation gives rise to rapid coagulation can be found experimentally; this concentration is referred to as the critical coagulation concentration. The exact concentration at which the particles would experience no repulsion barrier would be expected to depend on the the nature of the sol and temperature as well as on the surface electric charge and the nature of the electrolyte and the dispersion medium. For sols in water, however, certain regularities are immediately apparent.

![Image](image.png)

**Fig. 2.4.** Kaolinite colloids mainly [Colloid Mobilization and Transport in Saturated Porous Media, Colorado uni]

More complex coagulation behaviour is observed with some colloidal systems, like kaolinite suspensions, where the particles are so heterogeneous that they can
have charges of different sign at different sites of the surface allowing attractions to occur by electrostatic (Coulombic) interactions. However, it is more common in real systems to encounter mixture of particles with different surface characteristics. It is then possible for some group of particles to be of opposite sign to another one, when immersed in a homogeneous electrolyte solution.

The interaction between surfaces resulting from those surfaces having significantly different charge status is called heterocoagulation. It is relevant to many technological and industrial situations, like paint and ink-making and in surface coating generally.
2.2 Interaction between colloidal particles

Colloids are generally too large to be affected by quantum effects. However, they are light enough to be affected by the thermic motion happening in the suspension. Colloidal interactions are responsible for influencing the transport properties of colloidal suspensions, such as gradient diffusivity and also viscosity, and the thermodynamic properties such as the osmotic pressure, which is a key property in ultrafiltration processes.

The following forces play an important role in the interaction of colloid particles:

2.2.1 Excluded Volume Repulsion:

This refers to the repulsive force generated between the particles when they come close to each other (due to overlap of electron gas of the two particles). It can also refer to the impossibility of any overlap between hard particles. This is a short-range force [Diehl et al, 1996].

2.2.2 van der Waals Forces:

This is due to dipole-dipole interaction. Even if the particles don't have a permanent dipole, there could be fluctuations of the electron gas giving rise to a temporary dipole. So these types of forces are always present, although possibly at lower magnitude than others.

Furthermore, forces that deal with fixed or angle-averaged dipoles (Keesom forces) and free or rotation dipoles (Debye forces) as well as shifts in electron
cloud distribution (London Forces) are named after the Dutch chemist Johannes Diderik van der Waals.

The potential energy due to van der Waals effect between two colloidal particles of the same material immersed in a fluid is always negative (i.e. the force is attractive) and its magnitude decreases with about the second power of the separation between particles (the details depend on geometry and separation distance).

2.2.3 Entropic Forces:

An entropic force acting in a system is a macroscopic force whose properties are mainly determined not by the character of a particular underlying microscopic force (such as electromagnetism), but by the whole system's statistical tendency to increase its entropy. According to the second law of thermodynamics, a system evolves to a state in which entropy is maximized. This can result in effective forces even between hard spheres.

Entropic forces take place in the physics of gases and solutions, where they generate the pressure of the ideal gas and the osmotic pressure of a dilute solution, and in colloidal suspensions, where they are responsible for the crystallization of hard spheres [Lexico, 2006]. The packing of particles at a high concentration leads to an entropic pressure tending to disperse them, so the higher the entropic force the higher dispersion.
2.2.4 Steric Forces:

The Steric effects result from the fact that each atom within a molecule occupies a certain amount of space. If atoms are brought too close together, there is an associated cost in energy due to overlapping electron clouds, and this may affect the molecule's preferred shape (conformation) and reactivity.

Steric forces between polymer-covered surfaces or in solutions that contains non-adsorbing polymer can modulate interparticle forces, producing an additional steric repulsion force (which is predominantly entropic in origin) or an attractive 'depletion' force between them (which results from particles overlap causing the total volume accessible to the polymer to increase. It is this increase in free volume that causes an effective attraction) [Bolhuis, 1996].

2.2.5 Electrostatic Interaction:

The Coulomb potential is an effective pair potential that describes the interaction between two point charges. It acts along the line connecting the two charges. It is given by the equation:

\[ V_{\text{Coulomb}} = \frac{1}{4\pi\varepsilon_0} \frac{q_1 q_2}{r} \]  

[2.1]

where \( r \) is the distance between two ions (or what is represented as ion point charge), \( q_1 \) and \( q_2 \) the electric charge in coulombs carried by charge 1 and 2 respectively, and \( \varepsilon_0 \) is the electrical permittivity of space. The prefactor, \( 1/4\pi\varepsilon_0 \), is termed the electrostatic constant, or Coulomb's constant, \( k_c \), it has a value of \( \approx 9 \times 10^9 \text{Nm}^2\text{C}^{-2} \) (also mF\(^{-1}\)).
Colloids can be made so that they carry a charge. The Coulomb potential is proportional to $1/r$. However, if there are solvent particles with a charge opposite to that of the colloids, they arrange themselves and assemble around the colloids and screen the repulsion.

![Coulomb Potential](image)

**Fig. 2.5. The Coulomb potential:** The (green) bottom curve represents the interaction between some two particles of opposite charge; while the (red) top curve represents the interaction of particles of same charge [Wasser Manual 2000-2003, modified]

The repulsive force due to Coulombic interactions between colloidal particles leads to a positive potential energy, which decreases roughly exponentially with distance.

The force between the colloidal particles can be calculated as the derivative (with respect to separation distance between the particles) of the total potential energy curve.
2.3 The Electrical Properties of Colloids

The particles of a colloid selectively absorb ions and obtain an electric charge. All of the particles of a given colloid take on the same charge (either positive or negative) and thus are repelled by one another. If an electric potential is applied to a colloid, the charged colloidal particles move toward the oppositely charged electrode; this migration is called electrophoresis.

If the charge on the particles is neutralized, they can precipitate out of the suspension. A colloid can be precipitated by adding another colloid with oppositely charged particles; the oppositely charged particles are attracted to one another, coagulate, and precipitate out. Addition of soluble ions can precipitate a colloid; the ions in seawater precipitate the colloidal silt dispersed in river water, forming a delta.

A method developed by F. G. Cottrell reduces air pollution by removing colloidal particles (e.g., smoke, dust, and fly ash) from exhaust gases with electric precipitators. Particles in a lyophobic system are readily coagulated and precipitated, and the system cannot easily be restored to its colloidal state. A lyophilic colloid does not readily precipitate and can usually be restored by the addition of solvent.
2.3.1 Electrophoresis

Electrophoresis is an electrokinetic phenomenon. It was discovered by Reuss in 1809. He observed that clay particles dispersed in water migrate under influence of an applied electric field.

Generally, electrophoresis refers to the motion of dispersed particles relative to a fluid under the influence of an electric field that is space uniform. Alternatively, similar motion in a space non-uniform electric field is called dielectrophoresis.

Electrophoresis occurs due to the fact that particles dispersed in a fluid almost always carry an electric surface charge. An electric field exerts electrostatic Coulomb force on the particles through those charges [Hunter, 1989].

2.3.2 The Electrical Double Layer

The particles in a colloid are almost always electrically charged. This charge on the particle is balanced by an opposite charge in the surrounding fluid. This effect can be contributed to the adsorption of some of the fluid ions onto the particle surface. If the number of adsorbed anions exceeds the number of adsorbed cations, the surface would gain total negative electric charge. The dissociation of the surface chemical group might be another possible mechanism leading to surface charging [Lyklema, 1995].

The charge in the fluid is in the form of free ions. There is a region around each particle where the particle charge attracts the free ions to form an electrical cloud called the electrical double layer.
Figure 2.6 below shows the charge on the particle distributed over its surface and balanced by the total charge in the double layer in which there is an excess of positively charged ions (counter ions).

Fig. 2.6. The negatively charged particle is surrounded by positive ionic atmosphere

The earliest model of the electrical double layer is usually attributed to Helmholtz (1879) [Lexico, 2006]. Helmholtz treated the double layer mathematically as a simple capacitor (may be called a molecular condenser), based on a physical model in which a single layer of ions is adsorbed at the surface.

Helmholtz equations were interpreted by Perrin as implying a simple charge distribution in the solution, opposite to that on the solid (Figure 2.7.a). The equations for the electrical potential as a function of distance into the solution can readily be solved for this simple model of the double layer. This way they were able to explain some features of the behaviour of electrical double-layer systems [Hunter, 2001].
Chapter 2

(Fig.2.7. The electrical double layer:
(a) According to Helmholtz model, (b) The diffuse double layer resulting from thermal motion (Gouy-Chapman) model

The success of the kinetic theory of molecular behaviour made it clear that the Helmholtz model was unrealistic – especially in the treatment of the electric charge in the solution. Since the metal, for instance, is an electric conductor it is reasonable to assume that the charge on it is confined to the surface and that that surface can be regarded as a surface of constant potential. In the solution, on the other hand, ions of opposite sign predominate over ions of the same sign but the latter are not completely excluded from the surface region (Figure 2.7.b).

Later Louis G. Gouy and David L. Chapman (1910-1913) made significant improvements by introducing a diffuse model of the electrical double layer [Lexico, 2006], in which the potential at a surface decreases exponentially away from the surface to the fluid bulk, due to adsorbed counter-ions from the solution (Figure 2.7.b).
Figure 2.8 shows schematically what the electrostatic potential $\psi$ in the vicinity of a positively charged wall (particle) is expected to look like (The potential profile is similar to that near an ion in an electrolyte solution). The negative counterions (The red spheres in the figure) are attracted towards the positively charged wall by the electric field generated by the positive charges but they are also subject to thermal motion, which tends to distribute them uniformly through the surrounding medium.

The end result is typically a compromise in which a few negative ions are bound strongly to the particle surface and the concentration of the remainder falls off gradually away from the particle until it approaches the bulk concentration at distances of the order of some tens of nanometers.
The classical Gouy-Chapman model fails at highly charged DLs. In order to resolve this problem Stern O. Z. suggested the introduction of an additional internal layer, that is now called the Stern layer. This gave rise to the current classical electrical double layer; the Gouy-Chapman-Stern model, which combines the Helmholtz single adsorbed layer with the Gouy-Chapman diffuse layer. The attached counter-ions in the Stern layer and the charged atmosphere in the diffuse layer are what we now refer to as the double layer. Important approximations used in this model are [Lyklema, 1995]:

- Ions are effectively point charges.
- The only significant interactions are coulombic.
- Dielectrical permittivity is constant throughout the double layer.
- Viscosity of fluid is constant above slipping/shear plane.

The charge arrangement (diffuse electrical double layer) around the particle and its extent depends on the electrolyte concentration: increasing electrolyte concentration causes the diffuse double layer to shrink closer in to the particle, so that the electrostatic potential falls off more quickly with distance, as can be seen in Figure 2.9 below. This behaviour is sometimes called 'double layer compression'.
Fig. 2.9. Influence of electrolyte concentration on electrostatic potential in relation to distance

The nature in which the double layer surrounding two colloid particles interact with each other when they come together is more important than the single double layer.

When two colloid particles move toward one another, the double layer can be thought of as screening the charges on the colloid particles. At close separation, the screening is incomplete and each particle sees each other as a partially charged particle of the same sign. Therefore the particles will repel each other. This mechanism by which colloid particles may repel each other is an important property of a colloid.

Virtually all colloids in an aqueous dispersion acquire a surface charge and hence an electrical double layer. The Gouy–Chapman model gives the simplest description of an electrical double layer which comprises a charged surface and a
diffuse layer of counter ions, treated as point charges, in the solution. The
distribution of the charges in the solution is described by the Poisson–Boltzmann
equation (PBE).

### 2.3.3 Gouy-Chapman Electrical Double Layer Model

A flat surface is considered. The charge on that surface influences the ion
distribution in nearby layers of the electrolyte. The electrostatic potential \( \psi \), and
the volume charge density \( \rho \), are related by the Poisson equation – which reads in
one dimension as:

\[
\frac{d^2 \psi}{dx^2} = \frac{-\rho}{\varepsilon}
\]

where \( \varepsilon \) is the permittivity (dielectric constant) of electrolyte.

Here \( \Psi \) varies from \( \Psi_0 \) at the flat surface to \( \theta \) in bulk solution. Thus, we can relate
the charge density at any given point to the potential gradient away from the
surface.

The ion distribution in the charged surface region is determined by (i) temperature,
and (ii) the energy required \( w_i \) to bring the ion from an infinite distance away
(where \( \psi = 0 \)) to the region where the electrostatic potential is \( \psi \). This distribution
is given by a Boltzmann equation:

\[
c_i = c_i^0 \exp\left(-\frac{w_i}{k_B T}\right)
\]
$c_i^0 =$ concentration of ions of type $i$ in bulk solution.

$w_i = z_i e \psi$, the energy expended in bringing an ion from an infinite distance from the surface to a point where the potential is $\psi$.

$z_i =$ valency of ion species $i$,

$e =$ electron charge.

The volume charge density at $\psi$ is:

$$\rho = \sum_i c_i z_i e$$

[2.4]

The combination of this with the Poisson equation gives the Poisson-Boltzmann equation:

$$\frac{d^2 \psi}{dx^2} = -\frac{1}{\varepsilon} \left( \sum_i c_i z_i e \right)$$

[2.5]

In principal, $\psi$ and all other electrostatic properties can be evaluated for a given surface charge distribution (Neumann boundary condition) or surface potential (Dirichlet boundary condition).

### 2.3.4 Colloids in the DLVO theory frame

The DLVO theory (named after Derjaguin, Landau, Verwey and Overbeek who developed at the 1940s) explains the stability of colloids by looking at two opposing forces acting upon colloidal particles. These two forces are the electrostatic repulsion explained by the double layer model and the Van der Waals forces which are weak attractive forces between particles.

This theory explains the tendency of colloids to agglomerate or remain in a stable state of dispersion by combining the two forces. The net interaction effect is the result of the subtraction of the attraction force from the repulsion force. If the net
value is positive a repulsion effect will be experienced, otherwise agglomeration process will take place [Romo & Pitts, 1998].

In many cases we can change the environment to either increase or decrease the energy barrier, depending on aims. Several methods can be used to achieve this, such as changing the ionic environment, or pH, or adding surface active materials to directly affect the charge of the colloid. In each case, “zeta potential” measurements can indicate the impact of the alteration on overall stability [Zetameter inc., 2007].

2.3.5 Zeta Potential

The voltage drop across the electrical double layer is an important parameter for a colloid. This voltage drop at the end of shear layer or start of diffusion layer, known as the zeta potential (ZP), varies depending on the properties of the colloid. For example, adding salt to a colloid shrinks the electrical double layer, and reduces the zeta potential [Colloidal Dynamics Info. 2005].

Zeta potential and particle size are key indicators of the way colloids act both in storage and in use. In fact, the particle zeta potential influences the effective size of the particles in the colloid, so measuring both parameters simultaneously (particle size and zeta potential) makes particle characterization much more reliable.

As demonstrated in figures 2.10; by increasing the natural Zeta Potential of the colloidal particles, the overall interaction energy can be given a higher dispersion effect.
Fig. 2.10. Net Interaction Energies at low and high Zeta Potential

The natural zeta potential typically found in colloids in aqueous suspension ranges from -14 mV to -30 mV. At negative potential values higher than -30 mV enough repulsion occurs to favor a stable dispersion. The more negative the potential value, the stronger the dispersion effect (Figure 2.11). For values ranging between -45 mV and -70 mV stable dispersions are guaranteed [Romo & Pitts, 1998].

Fig. 2.11. Simplified diagram of particle interaction at low and high Zeta Potential
As the zeta potential approaches zero, the repulsion effect is lost and agglomeration begins. For values ranging from -10 mV to -15 mV a threshold of agglomeration is observed, and from values between -5 mV to +5 mV strong agglomeration occurs [Riddick, 1961].

2.3.6 The Conductivity of Colloids

Since most colloid particles are charged they contribute some conductivity to the solution. The conductivity measurements are important because they detect the presence of electrolyte and indicate roughly the amount and percent in a given colloid.

For instance, if dialysis is performed, the degree of purity and the extent of dialysis can be checked by conductivity measurement. Purer colloids have specific conductivity from about $10^{-4}$ to $10^{-5}$ rec. ohm to as low as $3 \times 10^{-6}$ rec. ohm. But if the colloids are contaminated with electrolytes, the specific conductivity lies between $10^{-2}$ to $10^{-3}$ rec. ohm.

But conductivity measurements cannot give the amount of impurities which do not conduct electricity. Sometimes, the conductivity measurement can be used to give information about the association of particles in colloidal solution.

2.3.7 The Influence of Electrolytes on the Charge of Colloids

By adding small quantities of electrolyte to a colloidal solution, the mobility of the particles may either increase or decrease. This means that the electrolytes may either increase or decrease the charge of the particles.
The effect of different electrolytes upon the same colloids was investigated several decades ago. The following rules were found to apply generally:

- Particles carrying a 'negative' charge are easily neutralized by acids.
- Particles carrying a 'positive' charge are easily neutralized by alkaline.
- Polyvalent cations strongly influence negatively charged particles, but the corresponding anions have little influence on the charge.
- Polyvalent anions have a strongly influence on the mobility and charge of positively charged particles, but the cations present in the solution are unimportant.

In some cases, adding the salt causes the mobility of colloids to decrease then after further addition of salt, the particles may move in the opposite direction. The sign of the charge can be changed.

This electrical property is useful in order to get rid of undesirable colloids even though it is quite difficult to separate the colloids in practice because a colloidal system is a complicated system. Nevertheless, this is an area of significant research interest.
Chapter 3

Electrostatic Interactions and Poisson-Boltzmann Equation

3.1 Introduction

The Debye-Huckel Theory, which we discuss later, is a continuum approach for molecular systems consisting of proteins or other complex macromolecules lying in ionic solutions. This continuum approach may be particularly suitable for molecular dynamics or Brownian dynamics simulations [Davis et al 1990, Wang et al 2008], when the electrostatic force is the dominant force in determining the behaviour of the system.

Continuum models of molecules in ionic solutions, proposed first in 1923 by Debye and Huckel, are increasingly important tools for studying electrostatic interactions. Since the electrostatic behaviour contributes to the structure, binding properties, as well as the kinetics of complex molecules such as proteins, modelling these interactions accurately is an important problem in biophysics and many other fields.

The fundamental equation arising in the Debye-Huckel theory is a three-dimensional second order nonlinear partial differential equation describing the electrostatic potential $\Phi(r)$ at a field position $r$. 
3.2 Gauss' law

The well known Gauss' law is a law relating the distribution of electric charge to the resulting electric field. For free space or vacuum, it is given in its differential form by:

\[ \nabla \cdot \vec{E}(\vec{r}) = \frac{\rho(\vec{r})}{\varepsilon_0} \]  

[3.1a]

where \( \vec{E} \) is the electric field and \( \rho \) is the electric charge density.

Or, using the relation \( \vec{E} = -\nabla \psi \) it can be transformed into a Poisson equation:

\[ \nabla \cdot \nabla \psi = -\frac{\rho}{\varepsilon_0} \]  

[3.1b]

where \( \Psi \) is the electric potential.

3.3 Debye-Huckel theory and the Poisson-Boltzmann equation

Debye and Huckel proposed in 1923 a continuum method for the calculation of electrostatic free energy of small spherical ions in an ionic solution. In their method, the ionic solution is treated as a continuum with a dielectric constant, and a partial differential equation governing the electrostatic potential is developed based on Gauss' law and the Boltzmann distribution law. This method is limited to low electrostatic potentials.
The Debye-Huckel theory is more recent than its counterpart for diffuse double layers at flat surfaces, the Gouy (or Gouy-Chapman) theory. However, Gouy-Chapman theory is more general than the Debye-Huckel theory in that it is valid also for high potentials but more limited in that it is restricted to flat surfaces [Lyklema, 1995].

3.3.1 The Debye-Huckel Model

In this model, the solvent with dielectric constant $\varepsilon$, is assumed to contain mobile ions. Assuming that all mobile ions are univalent for simplicity, we can treat them as positive and negative ions with charge $+e$ and $-e$, where $e$ is the charge of an electron (Higher valence ions can be treated in a similar fashion).

The electrostatic potential satisfies Gauss' law in this model. In differential form this yields a separate Poisson equation

$$\nabla^2 \psi(\vec{r}) = -\frac{\rho(\vec{r})}{\varepsilon}$$

[3.2]

where $\nabla^2$ is the Laplace operator ($= \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$). In order to use these equations to determine the potential $\Psi(\vec{r})$, the charge density functions $\rho(\vec{r})$ must be defined.
3.3.2 Gauss’ law and the Boltzmann distribution law

Define a coordinate system in three-dimension space, \( r = (x, y, z) \). The molecule is represented by a series of \( N_m \) charges \( q_i \) at positions \( r_i \), where \( q_i = z_i e, z_i \in \mathbb{R}, i=1, \ldots, N_m \). Assume that the bulk concentration of ions is \( n \) per cubic centimeter for each of the two sets of ions present, one of charge \(+e\), the other of charge \(-e\). The concentration of one type of ion then is assumed to follow the Boltzmann distribution law:

\[
n_i = n_i^0 \exp\left(-\frac{w_i(\vec{r})}{k_B T}\right)
\]  \[3.3\]

where \( T \) is the absolute temperature, \( k_B \) is Boltzmann's constant, \( w_i(\vec{r}) \) is the work required to move the ion of type \( i \) from \( |r| = \infty (\Psi(\vec{r}) = 0) \) to \( \vec{r} \), and \( n_i^0 \) is the bulk concentration of ions of type \( i \).

We will assume that the only work done in bringing the ion near the surface is the electrical work done on or by the ion as it moves in response to the field. This ignores the energies involved in moving aside other ions or creating a hole in the solvent, or any effect which the ion might have on the local structure of the solvent or the distribution of other ions.

Since we have only two types of ions in our model, we have simply

\[
 w_1(\vec{r}) = +e\psi(\vec{r}), \quad w_2(\vec{r}) = -e\psi(\vec{r}) \]
\[3.4\]

for the positive and negative ions, respectively. Therefore, the Boltzmann distribution law applied here gives:
\[ n_+ = n \exp(-e\psi(\vec{r})/k_B T), \quad n_- = n \exp(+e\psi(\vec{r})/k_B T) \quad [3.5] \]

where we assume that \( n_+ = n_- = n \), it turns out that this is not a very serious restriction because in most situations of interest in colloid science, the behavior of the system is governed almost entirely by ions of sign opposite to that of the surface [Hunter, 2001]. The charge density will then be given by:

\[ \rho(\vec{r}) = n_+ e - n_- e = -2n e \sinh \left( \frac{e\psi(\vec{r})}{k_B T} \right) \quad [3.6] \]

And Gauss' law then becomes:

\[ \nabla^2 \psi(\vec{r}) = -\frac{\rho(r)}{\varepsilon} = \left( \frac{2n e}{\varepsilon} \right) \sinh \left( \frac{e\psi(\vec{r})}{k_B T} \right) \quad [3.7] \]

### 3.3.3 The Debye-Huckel parameter

The ionic strength of the solution is defined as

\[ I_s = \frac{1}{2} \sum_{i=1}^{N_I} c_i z_i^2 \quad [3.8] \]

where \( N_I \) is the number of different types of ions, and \( c_i \) is the molar concentration of ion type \( i \) with charge \( q_i = z_i e \), the valency \( z_i \) may take positive or negative values. For this model, lets assume that \( N_I = 2 \), \( z_1 = z_2 = 1 \), and \( c_1 = c_2 = 1000 n/NA \), where \( NA \) is Avogadro's number. The ionic strength is then
\[ I_s = \frac{1}{2} \sum_{i=1}^{N} c_i z_i^2 = \frac{1000 \, n}{N_A} \]  \[3.9\]

This yields \( n = I_s N_A / 1000 \), and with this we can rewrite the equation as

\[ \nabla^2 \psi (\vec{r}) = \left( \frac{2N_A e I_s}{1000 \varepsilon} \right) \sinh \left( \frac{e \psi (\vec{r})}{k_B T} \right) \]  \[3.10\]

With the Debye-Huckel parameter \( \kappa \) defined to be:

\[ \kappa = \left( \frac{2N_A e^2 I_s}{1000 \varepsilon k_B T} \right)^{1/2} \]  \[3.11\]

we can write the equation in final form as

\[ \nabla^2 \psi (\vec{r}) = \kappa^2 \left( \frac{k_B T}{e} \right) \sinh \left( \frac{e \psi (\vec{r})}{k_B T} \right) \]  \[3.12\]

### 3.4 Limitations of the Poisson-Boltzmann Equation

The PBE is a continuum mean field approach assuming point-like ions in thermodynamics equilibrium and neglecting statistical correlations [Borukhov and Andelman, 1997]. The viability of the PBE to model asymmetric electrolytes has been the subject of a number of studies [Craig and Widom, 1997]. The main criticism concerns can be summed as:
a) the arbitrary separation of the double layer into a compact and a diffuse region; and
b) the identification of $w_f = z_e \Phi$ to describe the diffuse double layer.

A proper statistical mechanical approach would lead to a unified description across the entire double-layer region with the finite size of the ions and molecules entering by way of the distribution functions for those species in the neighbourhood of the interface. It should be noted, however, that very close to a plane interface the distribution of ions and molecules is significantly affected by their size. They can not approach closer than a specific distance and the number of molecular centers at that distance is expected to be very high as the liquid presses up against the wall.

The $w_f$ value in the second point of criticism, which can be found in Boltzmann’s equation, is supposed to measure the total work done in bringing the ion from the bulk solution into some point in the double layer, in short (reversible) steps, where the effect of the ion on the rearrangement of all of the other ions (and dipoles) is taken into account after each step. To equate it with $z_e \Phi$ is to discount all of the ancillary effects of the ion and to assume that only the electrical work, estimated by bringing up an infinitesimal charge, is important. Fortunately, it turns out that many of the other effects tend to cancel one another out provided that neither $|\Phi|$ nor the electrolyte concentration is too large. Under those conditions the Poisson-Boltzmann equation remains quite satisfactory. At high concentrations, when it is likely to break down, the diffuse layer has a negligible effect on the double layer capacitance, so deficiencies in the diffuse double layer theory are not apparent. In colloidal systems the same situation applies: at very high electrolyte concentrations, double-layer effects become much less significant and the limitations of the PBE are not too serious [Hunter, 2001].
Despite the limitations in its assumptions, the PB approach remains to be a valuable tool in quantifying colloidal interactions for workers in EIIs field. When applicable, both MC and PB approaches can give quantitative agreement with experimental results for EIIs in solution [Sharif et al., 2002].
Chapter 4

Solutions of the Governing Equations of Electrostatic Interactions

4.1 Introduction

During the past half-century or so, the growth in power and availability of digital computers has led to an increasing use of realistic mathematical models in science and engineering. Numerical analysis of increasing sophistication has been used to solve these more detailed mathematical models.

Boundary-value problems of mathematical physics occur in almost every engineering application. Different aspects are present, for instance, in structural analysis, heat transfer, fluid flow, electromagnetic fields, and they are indeed of great interest in all practical design problems.

In the design process, the designer tries to define, by successive hypotheses and approximations, suitable boundary-value problems and to find acceptably accurate solutions to them. In the past, valuable help for the designer was forthcoming from experimental data obtained from working systems. However, the ongoing increase in the complexity and the costs of experiments has greatly reduced the availability of experimental data. Thus the development of advanced technologies and the increase in dimensions and costs of many engineering systems have made necessary the development of more general and accurate computation techniques than what was previously available.
The analytical methods class is very broad and includes many algorithms and procedures. The major deficiency of the analytical method is the lack of generality. The classes of problems for which analytical solutions exist that can be considered somewhat general are by far the simplest ones and many algorithms are applicable only to two-dimensional and steady-state problems. Besides, algorithms for inhomogeneous and nonlinear cases are practically non-existent excepting for some simple and special problems. Even for the simplest systems, such as a spherical molecular surface containing a central charge, analytic solutions to the nonlinear PBE are unavailable and numerical methods are necessary. Another notable deficiency of analytical methods lies in the effort required in obtaining the field of solutions, such as developing special algorithms and discovering artifices [Chari and Silvester, 1980].

The deficiencies of analytical methods are eliminated to a large extent in numerical methods, which have come to the fore with the advent of computers. Numerical analysis can be used to compute (in an approximate way) the solution of differential equations, both ordinary differential equations and partial differential equations. Partial differential equations are solved by first discretizing the equation, bringing it into a finite-dimensional subspace. This can be done by a finite element method, a finite difference method, or a finite volume method. The theoretical justification of these methods often involves theorems from functional analysis. This reduces the problem to the solution of a set of algebraic equations.

Next, we will introduce some special problems where an analytical solution was possible. This will be followed by sections on each of the three major numerical approaches to deal with the electrostatic interactions' governing equations; namely; Monte Carlo method (MC), Finite Difference Method (FDM) and Finite Element Method (FEM). A brief description of each numerical method will be given with its advantages and disadvantages.
4.2 Approximate Approach to Solve Equations of Electrostatic Interactions

Analytical solutions to the linearized and nonlinear Poisson-Boltzmann equations are quite complex, even in the few simple situations for which they exist.

In special cases, analytical solutions to the linearized Poisson-Boltzmann equation can be explicitly constructed in different model regions separately and pieced together by enforcing continuity conditions at the region boundaries. In other situations, simplifying assumptions can be made which result in a single analytically solvable equation which governs the entire domain.

A spherical particle with uniform charge where the coordinate system is taken spherical and centred at the particle is one example of the first category. Here the PBE is defined in three regions, and then two sets of boundary conditions are added where each region connect to the others.

Complete solvent penetration is of the second category - An example is that of a long rod-shaped molecule, which the ionic solution is assumed to completely penetrate. In this case, one equation governs the entire domain and the molecule is represented by set of point charges.

In other cases, analytical solutions to the linearized form of the Poisson-Boltzmann equation have been given in slightly more complex situations in which a spherical molecular geometry is still required, but the spherical symmetry assumption on the charge distribution is relaxed. In the very special simplified
case of an infinite planar molecule, the Guy-Chapman theory can be used as an alternative to the nonlinear Poisson-Boltzmann model [Holst, 1994].

However, in the more general case without symmetries or other assumptions, even knowledge of existence and uniqueness of a solution, especially in the nonlinear case, is a difficult question. Without strong continuity assumptions on the coefficients, the standard potential theory [Kellog 1953] is not useful for proving that a unique solution exists. However, even with the knowledge that a unique solution exists, in most cases there remains no closed form expression for such a solution. Therefore, these solutions must be approximated numerically.

As an example on analytical solutions, let us consider the scenario of a spherical particle with uniform charge [Holst 1994; Tanford 1961]: A spherical molecule with spherically symmetric total charge $q$ on the molecule surface, immersed in a solvent containing mobile univalent ions (as in Figure 4.1).

Defining the coordinate system to be centred at the molecule, the radius of the molecule defining region $\Omega_1$ is denoted by $R$. The ions may approach only to a distance $a > R$, which defines the ion exclusion layer $\Omega_2$ around the molecule. The ionic solvent then lies in the region $\Omega_3$. The solvent dielectric constant in regions $\Omega_2$ and $\Omega_3$ is denoted by $\varepsilon_w$, while the molecule dielectric in region $\Omega_1$ is denoted $\varepsilon_m$. Since the charge $q$ is assumed to be evenly distributed over molecule surface of area $4\pi R^2$, the molecule has the uniform charge density:

$$\sigma = \frac{q}{4\pi R^2} \quad [4.1]$$
In spherical coordinates with spherical symmetry the linearized form of the Poisson-Boltzmann equation is easily seen to reduce to:

region $\Omega_1$: \[
- \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \psi (r) \right) = 0 , \quad r < R , \quad [4.2]
\]

region $\Omega_2$: \[
- \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \psi (r) \right) = 0 , \quad R < r < a , \quad [4.3]
\]

region $\Omega_3$: \[
- \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \psi (r) \right) + \kappa^2 \psi (r) = 0 , \quad r > a , \quad [4.4]
\]
where the zero source functions are a result of placing the charge on the molecule surface. For boundary conditions on $\Gamma_{12} = \Omega_1 \cap \Omega_2$ (at $r = R$), we must have:

$$\Psi_1(r) = \Psi_2(r), \quad \varepsilon_1 \left( \frac{d\psi_1}{dr} \right) - \varepsilon_2 \left( \frac{d\psi_2}{dr} \right) = -4\pi\sigma = \frac{-q}{R^2}, \tag{4.5}$$

whereas on $\Gamma_{23} = \Omega_2 \cap \Omega_3$ (at $r = a$), we must have:

$$\Psi_2(r) = \Psi_3(r), \quad \varepsilon_2 \left( \frac{d\psi_2}{dr} \right) = \varepsilon_3 \left( \frac{d\psi_3}{dr} \right), \tag{4.6}$$

It is quite easy to verify (by differentiating twice) that the general solution in each region is:

region $\Omega_1$: $\psi_1(r) = c_1 + \frac{c_2}{r}$, $\tag{4.7}$

region $\Omega_2$: $\psi_2(r) = c_3 + \frac{c_4}{r}$, $\tag{4.8}$

region $\Omega_3$: $\psi_3(r) = c_5 \frac{e^{-kr}}{r} + c_6 \frac{e^{kr}}{r}$, $\tag{4.9}$

The boundary and continuity conditions, and the requirement that $\Psi(r)$ be finite in region $\Omega_1$, give six conditions for the six constants. The resulting expressions for the solution in each region are:

region $\Omega_1$: $\psi_1(r) = \frac{q}{\varepsilon_\infty R} \left( 1 - \frac{R\kappa}{1 + \kappa a} \right)$, $\tag{4.10}$

region $\Omega_2$: $\psi_2(r) = \frac{q}{\varepsilon_\infty r} \left( 1 - \frac{r\kappa}{1 + \kappa a} \right)$, $\tag{4.11}$

region $\Omega_3$: $\psi_3(r) = \frac{qe^{\kappa a}}{\varepsilon_\infty (1 + \kappa a)} \frac{e^{-kr}}{r}$, $\tag{4.12}$
4.3 Numerical Approach

The field of numerical analysis, or computational mathematics, is concerned with several of the steps required to solve a scientific problem of current interest using modern computers, to be able to get specific results or some data of interest:

1. Statement of the physical problem as a governing system of equations.
2. Analysis of the properties of the governing system.
3. Construction and analysis of an approximating system.
4. Development and analysis of numerical methods for the approximating system.
5. Efficient implementation of the numerical methods on computers.

The degree of concern for a particular step usually depends on the particular area of specialization. Typically, this requires knowledge in physics, applied mathematics and numerical analysis, as well as sufficient computer background.

4.3.1 Monte Carlo Method

Numerical methods known as Monte Carlo (MC) methods can be loosely described as statistical simulation methods, where statistical simulation is defined in quite general terms to be any method that utilizes sequences of random numbers to perform the simulation.

Monte Carlo methods are important in computational physics and related applied fields, and have various applications from esoteric quantum chromodynamics calculations to designing heat shields and aerodynamic forms. These methods
have proven efficient in solving the integro-differential equations defining the radiance field. They are especially useful in studying systems with a large number of coupled degrees of freedom, such as liquids, disordered materials, and strongly coupled solids [CSEP, 1995].

In many applications of Monte Carlo the physical process is simulated directly, and there is no need to even write down the differential equations that describe the behaviour of the system of interest. However, this would be true assuming that the evolution of the physical system can be described by probability density functions (pdf).

There are, however, some important limitations of the method that must be kept in mind. These limitations include an inherent lattice anisotropy that manifests itself in various ways. The main disadvantage of this method is that accuracy is a function of the number of trials; it needs huge resources to perform reasonably - depending on the problem to be solved, which makes it useless for many applications in practice.

There have been rapid developments in the applications of MC in electrostatic interactions in the last twenty years. [Fushiki et al., 1991], [Diehl and Levin, 2005] and [Tavaresa et al., 2004] provide a good insight on the recent state of this field. It should be noted that a general trend of the literature involving MC applications in ELs field, does not introduce the MC method as a substitute to the PBE, but rather as a last resort in situations where the PBE may fails. It is more needed, however, in atomic scale simulations where atomic details are important, such in some biological simulations.
4.3.2 Finite Difference Method

Finite difference schemes were one of the first numerical methods to be widely used. The first application to two-dimensional problems was made in 1908 by Runge. There was a parallel development of methods of solutions for the large algebraic equations resulting from the finite difference schemes.

In the finite difference approximation of a differential equation, the derivatives in the equations are replaced by difference quotients which involve the values of the solution at discrete mesh points of the domain. The resulting discrete equations are solved, after imposing the boundary conditions, for the values of the solution at the mesh points.

However, the use of finite difference methods on irregular grids has not proved very successful, so that regular grids are the only ones in practice to date. As a consequence, severe difficulties are encountered in solving many problems using finite-difference schemes, and therefore their efficiency is considered limited. This is essentially due, apart from other less important problems, to geometrical reasons related to the fitting of the grid to the shapes of boundaries and interfaces involved. In fact, a regular grid is not suitable for problems with very steep variations of fields. The grid must indeed be denser in regions of high field gradients, and this requires either a very large number of nodes, so that computation time and memory requirements are significantly increased, or a complex algorithm to increase the density of the grid artfully. Moreover, a regular grid is not suitable for curved boundaries or interfaces, because they intersect gridlines obliquely at points other than nodes. This may not be a big problem under Dirichlet boundary conditions, but poses difficulties under Neumann boundary conditions or under interface conditions involving normal derivatives.
These situations require sophisticated interpolation schemes which are difficult to implement in an automated form, and complicate the solution of algebraic equations resulting from the discretization [Chari and Silvester, 1980]. In spite of these shortcomings, finite-difference schemes, in their traditional version, monopolized the area of numerical methods in electrical engineering up to 1970s and led to many valuable results.

Among numerical methods to solve PBE, the finite difference method (FDM) [Warwicker and Watson, 1982] is one of the most widely used. Ionizable atoms are assigned to grid points and the electrostatic potential at each grid point is calculated using the finite difference approximation of the PBE. The accuracy of the results is highly dependent on grid spacing, while the computational cost increases steeply with the number of grid points. One approach to reduce the cost is called focusing [Gilson et al, 1988], in which the mesh of the grid is reduced only in the vicinity of ionizable groups of particular interest with potentials from coarser grids used as initial guesses. Another is the adaptive space-subdivision approach [Baker et al., 2001; Holst et al., 2000].
4.3.3 Finite Element Method

The finite element method is a numerical technique for obtaining approximate solutions to problems of mathematical physics. The method has a history of more than sixty years. It was first proposed in the 1940s and its use began in the 1950s for aircraft design [Jin, 1993]. Numerical solutions of the PBE that have used the finite difference method (FDM) have not been flexible enough to allow for the changes in size, shape and geometry of the system under consideration.

One important advantage of the FEM over the FDM is that while the latter requires the use of regular cells, the former allows geometrically irregular elements. This permits a more accurate description of curved or irregular boundaries. The principal disadvantage of the FEM has been its computational complexity, which arises from the use of large matrices. This has been overcome by the advances in computers and the use of special algorithms.

In the finite-element method, the field region is subdivided into subregions (elements) where the unknown quantities, such as, a scalar or a vector potential, are represented by suitable interpolation functions that contain, as unknowns, the values of the potential at respective nodes of each element. The minimization of the energy functional by use of such interpolation functions generates an algebraic system of equations, as in the finite-difference methods, and the potential values at the nodes can be determined by direct or iterative methods.

For in depth description of the FEM, please refer to some of the more detailed books on the subject like [Zienkiewicz 1983; Smith & Groffith 1998].
In the last thirty years, the FEM proved to be very useful in many fields. Typical strengths of finite element methods are that computational grids can resolve small levels of detail and that an approximation can be of different degrees of smoothness in different sections of the region of interest. Elements can have various shapes, and can be easily adapted to any shape of boundary.

The literature on the FEM applications has increased rapidly especially in the last twenty years, in almost every technical field. This was also noticeable in the EIs applications field. Selected examples of contributions to this area; [Carnie et al, 1994], [Bowen and Sharif, 1997], [Pujar and Zydney, 1997], [Bowen et al, 1999], [Sharif et al, 2003] and [Das and Bhattacharjee, 2004] – which shows how the field has developed and how it can be extended to cover different problems with different settings.
Chapter 5

Mathematical Modelling and Governing Equations

5.1 Introduction

Due to the difficulty of describing the equilibrium distribution of the electrolytic ions even via numerical simulation carried out on modern computers, this has led to the development of approximate treatments of the equilibrium properties of `ionic atmospheres' surrounding static charge distributions. One of the most widely utilized approximate descriptions is the Poisson-Boltzmann Equation, which can be motivated heuristically as a modification of Poisson's Equation.

The viability of the PBE to model asymmetric electrolytes has been the subject of a number of studies [Craig and Widom, 1997]. The PBE is a continuum mean field approach assuming point-like ions in thermodynamics equilibrium and neglecting statistical correlations [Borukhov and Andelman, 1997]. Even so, in comparison with Monte Carlo (MC) simulations it has been found that both MC and PB approaches can give quantitative agreement with experimental results for EIs in solution [Sharif et al., 2002]. It was concluded that PB theory was an excellent approximation for ion density profiles except for the interaction of divalent cations with specific binding sites. The agreement for free energy differences was in part due to the cancellation of errors. Others have concluded that while MC and PB calculations give estimates for both mono and divalent concentrations at the surface of strong polyelectrolytes, care must be exercised in their use as predictive
methods [Pack et al., 1999]. In this context it should also be noted that the full
(non-linear) PB approach is notably more reliable for systems with divalent ions
than the linearised PB [Bowen and Sharif, 1997].

Overall, despite limitations in its assumptions, the PB approach remains a valuable
means of quantifying colloidal interactions for workers in EIs fields. This is
especially true if comparison with experiment is made in terms of zeta-potentials so
that the condensation at the surface does not need explicit consideration [Sharif et
al., 2002].
5.2 Poisson-Boltzmann Equation

The electrostatic potential $\psi(\vec{r})$ and the volume charge density $\rho(\vec{r})$ which is the excess of charges of one type over the other, at any point $\vec{r}$ are related by the Poisson equation:

$$\nabla^2 \psi = -\frac{\rho(\vec{r})}{\varepsilon}$$  \hspace{1cm} [5.1]

$$= -\frac{e}{\varepsilon} (z_- c_- + z_+ c_+)$$

$\varepsilon$ = the permitivity.

e = electron elementary charge.

c_± = local concentration of ions in bulk solution.

$z_±$ = their valances.

Here $\Psi$ varies from $\Psi_0$ at the surface to $\theta$ in bulk solution. Thus, we can relate the charge density at any given point to the potential gradient away from the surface. Each ion density in the solution obeys a Boltzmann distribution and adjusts to the presence of the electric potential:

$$c_i = c_i^0 \exp(-\frac{z_i e \psi(\vec{r})}{k_B T})$$  \hspace{1cm} [5.2]

$k_B$ = Boltzmann constant,

c_i^0 = concentration of ions far from the particle concerned,

$T$ = the absolute temperature.

Combining the Boltzmann distribution with the Poisson yields the Poisson-Boltzmann Equation (PBE):
\[ \nabla^2 \psi = -\frac{\sigma_\psi}{\varepsilon} \]  \hfill [5.3]

where the space charge density: \( \sigma_\psi = \sum_i c_i^0 z_i e \exp\left(-\frac{z_i e \psi(\vec{r})}{k_B T}\right) \)  \hfill [5.4]

This can be written for a two-dimensional electrostatic layer in cylindrical coordinates as

\[
\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \psi}{\partial r} \right) + \frac{\partial^2 \psi}{\partial z^2} = -\frac{\sigma_\psi}{\varepsilon} \]  \hfill [5.5]
5.3 Governing Equations

The normalised Poisson-Boltzmann equation for a two-dimensional electrostatic double layer in cylindrical co-ordinates has the form:

\[
\frac{\partial^2 \Psi}{\partial R^2} + \frac{1}{R} \frac{\partial \Psi}{\partial R} + \frac{\partial^2 \Psi}{\partial Z^2} = -\sigma \tag{5.6a}
\]

The equation for the three-dimensional electrostatic double layer in Cartesian co-ordinates is of the form:

\[
\frac{\partial^2 \Psi}{\partial X^2} + \frac{\partial^2 \Psi}{\partial Y^2} + \frac{\partial^2 \Psi}{\partial Z^2} = -\sigma \tag{5.6b}
\]

For the normalized PBE, the dimensionless co-ordinates are defined using the following substitutions:

The dimensionless co-ordinates \( R = \kappa r, \ Z = \kappa z, \ X = \kappa x, \ Y = \kappa y \),

The dimensionless space potential \( \Psi = e\psi/k_B T \),

And the dimensionless space charge density \( \sigma = \frac{1}{2} \sum z_i C_i, \exp(-z_i \Psi) \) \tag{5.7}

where \( r, x, y \) and \( z \) are the dimensional co-ordinates, \( e \) is the elementary electric charge, \( \psi \) is space potential, \( k_B \) is Boltzmann constant, \( T \) is the absolute temperature, \( C_i = c_i^0/I \) is the relative concentration (\( I = \frac{1}{2} \sum z_i^2 c_i^0 \) is the ionic strength of the electrolyte) and \( \kappa \) is the Debye length which has the following form (\( N_A \) is Avogadro’s number):
In situations where the system is in contact with a symmetric 1:1 electrolyte reservoir (e.g. Na\(^+\)Cl\(^-\)), \(c_i^0 = c^0\) is the electrolyte concentration in the reservoir, Eq.[5.7] is reduced to

\[ \sigma = \sinh \Psi \] \hspace{1cm} [5.9]

Here \(z_\pm = \pm 1\) is inserted explicitly (which is the case of monovalent ions).

Equation [5.6] is a nonlinear partial differential equation with more than one spatial variable, which means that this equation has no analytical solutions and either must be solved numerically or requires further approximations.
5.4 Numerical Solution of the Normalized PBE

Equation [5.6] has been solved numerically to calculate the potential distribution using adaptive FEM combined with error estimation and mesh refinement [Bowen and Sharif, 1997].

We will consider for now a geometry representing a sphere approaching a pore. However, the analysis will be applied to various geometries in a similar manner, as will be demonstrated later on.

![Figure 5.1](image)

**Fig. 5.1.** AB, EF are Boundary inlet and outlet respectively; GH sphere surface; DE pore surface; CD planar surface. AB and BC natural boundary; boundaries AH and GF, z axis, line of symmetry

In order to solve the normalized PBE, it's necessary to define the potential $\Psi$ and the potential gradient $\partial \Psi / \partial N$ at the boundary $\Gamma$, $N = \kappa n$ is the outward normal direction from the boundary $\Gamma$. Axisymmetry of the geometry implies that derivatives with respect to the coordinates $R$ on the lines $AH$, $GF$ are assumed to be zero. The natural boundary conditions of the Neumann type on lines $AB$, $BC$ and $EF$ were satisfied within numerical error by appropriate choice of grid
dimensions. And the electric potentials within the sphere and the material surrounding the pore are constant.

The nondimensional parameters to be considered are the reduced potential $\Psi$, the scaled particle radius $Ka$, the sphere radius to pore radius ratio $\lambda$, and the closest approach $L=kh$, where $h$ is the centre line distance between the sphere surface and the pore entrance (the drop of line CD).

The FE method combined with Newton sequence technique has been used. Provided that a good initial guess is made using the Debye-Huckel solution, the Newton sequence usually converges within three iterations.

The free energy of the double layer is equal to the amount of work performed in building up the double layer around the colloid particle by some reversible and isothermal process.

The total free energy can be calculated when solving the PBE around a single colloidal particle using the free energy expression derived by [Loeb et al., 1961],

$$G = -\int_{S_P} dS \int_{0}^{\Psi_s} (\Psi') d\Psi$$  \hspace{1cm} [5.10]

where $G$ is the total free energy around a colloidal particle, $\Psi_s$ is the surface potential, $S_P$ is the surface area of the particle, and $\sigma_s$ is the surface charge density.

Equation [5.10] is inconvenient for numerical computation because $\Psi$, rather than $r$ and $z$, is the independent variable. Therefore, an equivalent expression for the total energy integral that involves only integrals over the volume of the ion
atmosphere has been used. Equivalent expression for the free energy, derived by Levine, reads

\[ G = -\int (\Delta \Pi + X) \, dv \]  

where \( \Delta \Pi = k_B T \sum_i (n_i - n_i(\infty)) \) is the osmotic pressure difference and \( X = \frac{e^2}{2} |\nabla \psi|^2 \) is the electrostatic free energy. Here \( n_i \) and \( n_i(\infty) \) are mean numbers per unit volume of ions in the double layer and in the bulk fluid, respectively.

Initial results will be expressed in terms of the dimensionless free energy \( G^* \), with

\[ G = -\frac{\varepsilon \pi \left( \frac{k_B T}{e} \right)^2}{\kappa} G^* \quad \text{(Cylindrical)} \]  
\[ G = -\frac{\varepsilon \left( \frac{k_B T}{e} \right)^2}{\kappa} G^* \quad \text{(Cartesian)} \]

where the dimensionless quantity \( G^* \) is given in our cylindrical coordinates for a symmetric 1:1 electrolyte system by

\[ G^* = \int_0^\infty \int_0^\infty [2(\cosh \Psi - 1) + |\nabla \Psi|^2] R dR dZ \]  

and for Cartesian coordinates for a symmetric 1:1 electrolyte system by

\[ G^* = \int_0^\infty \int_0^\infty \int_0^\infty [((\cosh \Psi - 1) + \frac{1}{2} |\nabla \Psi|^2] dX dY dZ \]

To obtain values of \( G^* \), Eq.[5.13] has to be evaluated numerically over the entire solution domain, by using the FE solution for \( \Psi \) and \( \partial \Psi/\partial R \) and \( \partial \Psi/\partial Z \) (or \( \partial \Psi/\partial X \), \( \partial \Psi/\partial Y \) and \( \partial \Psi/\partial Z \) for the 3D model). Here the equations will be solved for conditions of constant surface potential, which is expected to give the lower bound for the interaction.
The first physical quantity of interest is the free energy of interaction. This is defined as the change in the total free energy as the two surfaces are brought from infinity to their given configuration. Thus, the following dimensionless quantity is introduced:

$$\Delta G^*|_L = G^*|_L - G^*|_\infty$$ \[5.14\]

The interaction free energy between the sphere and the pore at a given distance $L$ can be written as

$$\Delta G^*|_L = G^*|_L - G_s^* - G_m^*$$ \[5.15\]

where $G_s^*$ is the dimensionless free energy for a single isolated sphere and $G_m^*$ is the dimensionless free energy for the isolated pore and planar surface.

The electrostatic force acting on the particles can be obtained by two methods. First, indirectly by differentiating Eq.\[5.14\] for $\Delta G^*(L)$ with respect to the separation distance $L$,

$$F^*(L) = -\frac{\partial \Delta G^*|_L}{\partial L}$$ \[5.16\]

Second, directly by integrating the stress tensor $T$,

$$T = \Delta \Pi + \varepsilon [\mathbf{EE} - \frac{1}{2} \mathbf{E} \cdot \mathbf{E} \delta]$$ \[5.17\]

over a suitable surface. Here $\mathbf{E} = -\nabla \psi$ is the electric stress; $\Delta \Pi$ is the difference in local osmotic pressure from that in the bulk electrolyte solution and it is related to the electrostatic potential in a symmetric 1:1 electrolyte system by

$$\Delta \Pi = 2n_b k_B T (\cosh \Psi - 1)$$ \[5.18\]

where $n_b$ is the bulk ion number density of the symmetric electrolyte.
To evaluate the force on the sphere, the following surface integral can be performed either on the sphere surface or on the midplane for the case of two identical spherical particles,

\[ F = \int_{s} T \cdot n \, ds \quad [5.19] \]

where \( n \) is the outward normal at the surface \( s \). The electric stress is calculated from the potential but the force on the sphere also includes a contribution from the osmotic pressure generated by the electric field; however, pressure variation due to the field at the sphere surface is normally cancelled by electrical effects.

The electrostatic interaction force \( F \) between two identical spheres, acting along their line-of-centres, is obtained by integrating the stress tensor over the midplane. The expression for the dimensionless force \( F^* \) [Sharif et al., 2003] for the 2D model is,

\[ F^* = \int_{0}^{\infty} \left[ 2 \cosh \Psi - 1 + \left( \frac{\partial \Psi}{\partial R} \right)^2 \right] R \, dR \quad [5.20a] \]

and assuming the z-axis is perpendicular on the midplane for the 3D model,

\[ F^* = \int_{0}^{\infty} \int_{0}^{\infty} \left[ 2 \cosh \Psi - 1 + \left( \frac{\partial \Psi}{\partial X} \right)^2 + \left( \frac{\partial \Psi}{\partial Y} \right)^2 + 2 \left( \frac{\partial \Psi}{\partial X} \right) \left( \frac{\partial \Psi}{\partial Y} \right) \right] \, dX \, dY \quad [5.20b] \]

where \( R \) is the radial coordinate along the midplane, \( X, Y \) are the axial coordinates spanning the midplane, \( Z \) is the coordinate normal to the midplane, both are scaled by Debye length \( \kappa^{-1} \), and the integrand is evaluated at the midplane \( Z=L/2 \), where \( L \) is the centreline distance between the sphere surfaces. For identical spheres, symmetry requires \( \frac{\partial \Psi}{\partial Z}=0 \) at \( Z=L/2 \) so the integrand is manifestly positive.
The dimensionless force acting on the sphere was obtained using two methods (Eqs. [5.16] and [5.20]). The first method requires the differentiation of the free energy of interaction, for which a set of data is required; the second method calculates the force directly with less computational effort. The force in dimensional form for both methods can be written as

\[ F = \varepsilon \pi \left( \frac{k_B T}{e} \right)^2 F^* \quad \text{(2D)} \quad [5.21a] \]

\[ F = \varepsilon \left( \frac{k_B T}{2e} \right)^2 F^* \quad \text{(3D)} \quad [5.21b] \]
5.5 Finite Element Method Implementation

The Finite Element Method used here, which involves formulating and assembling of partial differential finite element equations, uses the weighted residual concept and the Newton sequence technique to solve the resulting discrete system. Provided that a good initial guess is made, the Newton sequence will usually converge within three iterations [Eow et al., 2003]. The method of weighted residuals is actually a way of reducing the number of independent variables or the domain dimension. The basic idea of the method is to approximate the solution of the problem over a domain by a functional form called a trial function. The form of the trial function is specified but it has adjustable parameters within it. The trial function is chosen so as to give a good solution to the original differential equation.

The Galerkin method with nine-noded quadrilateral elements is used to reduce the order of the highest partial derivatives for 2D cases, as it was more convenient to use due to the availability of mesh generating software based on it. Figure 5.2 shows a typical nine-noded quadrilateral element used in the present work. Quadrilateral elements give solutions which are less sensitive to mesh design, and the nine-node Lagrangian element has been found very effective [Silvester and Ferrari, 1997]. Two-dimensional Lagrangian shape functions can be generated using products of one-dimensional shape functions. Within an element, potential components are approximated by quadratic functions defined at nine element

Fig. 5.2: Nine-node quadrilateral element
nodes; four at the vertices, four at the mid-side and an internal node (see figure 5.2). The sub-division of the problem usually leads to non-rectangular elements or elements with curved sides. The transformation from the parent element to a general quadrilateral of arbitrary shape with straight or curved sides can be generated by mapping the reference element into global coordinates.

The weighted residual concept is then used to approximate the solution function over each finite element domain. Care needs to be taken to ensure continuity of the dependent variables and their first partial derivatives in moving from element to element. Partial differential equations are, therefore, transformed into a set of ordinary differential equations in time, in matrix form, for each element. The second-order FE basis functions on each element are associated with nodal points and are applied to represent the variations of the field variables within the elements. Once such equations are formulated for all the elements, the global matrices are then assembled, resulting in a set of nonlinear simultaneous equations, which are then solved using an iterative method. Simple successive substitution of previous generated potential values in the iterative procedure fails to give convergence. Therefore, the very highly non-linear characteristic of the problem requires the application of special techniques to promote convergence, which can be achieved by utilising a weighting factor related to the previous updated potential values.

A 'mesh generator' is an automatic procedure for generating all the information in an element topology block. The information includes the coordinates of each node, the node numbers attached to each element and to the boundary elements. An adaptive remeshing technique for the solution of the Poisson-Boltzmann equation is employed here. The posteriori error estimator by Zienkiewicz and Zhu is utilised here to estimate the error in the potential gradient, providing the information to generate a new mesh to achieve the preset accuracy. A
mathematical description of the FE error estimation is provided by [Bowen and Sharif, 1997].

![Twenty-seven-noded 3D element](image)

*Fig. 5.3: Twenty-seven-noded 3D element*

For the three-dimensional model, 27-noded 'brick' elements were used in the present work; with eight nodes at the vertices, twelve at the middle of the edge-lines, six at the centre of the six surface planes and an internal node (see figure 5.3). Other element types were considered but the 27-noded element proved to be the most suitable after validation processes, as they had the best agreement with the reference data.

Integration of the results from the solution of Poisson-Boltzmann equation over volume gives the free energy of interaction of the particles at all distances. Differentiation of this free energy with respect to the distance results in the electrostatic force of interaction.
Chapter 6

Two-Dimensional Electrostatic Interactions Models

6.1 Introduction

This chapter presents and discusses the electrostatic interactions of a number of two-dimensional geometries and for different surface properties (fixed potential and/or surface charge); particularly: (i) of a charged single spherical particle and a charged wall; (ii) two interacting identical spherical particles; (iii) a chain of identical spherical particles; (iv) chain of identical spheres inside a chain of charged rings.

Calculations of the electrostatic force and free energy of interactions have been carried out for ranges of different values of parameters; sphere surface potential/sphere charge, sphere radius/tube radius ratio, sphere/wall potential.

The last case, of system of chain of spheres inside chain of rings, is of more interest in this chapter and will be the focus of the chapter, for both its importance - as it is more representative of many-body systems like arrays of spheres, and for its behaviour under specific conditions.

Occasionally, "reduced" or "dimensionless" is omitted when referring to variables that can be described as such, especially in later chapters. However, it should be implicitly understood by that point.
6.2 Electrostatic Interaction between Sphere and Wall

6.2.1 Problem Definition

The quantification of electrostatic effects of a single charged spherical particle at various distances from a charged wall is necessary in many applications as a comparative reference for similar systems.

For the geometry shown above, which represents a sphere at a distance from a wall (due to axisymmetry, only half of problem in 2D plane is considered), $\Psi = \Psi_s$ on the boundary $EF$ (which refers to the sphere surface) and $\Psi = \Psi_w$ on the boundary $CD$ (which refers to the planar surface of the wall). Axisymmetry of the geometry implies that derivatives with respect to the coordinates $R$ on the lines $AF$, $ED$ are assumed to be zero. The natural boundary conditions of the Neumann type on lines $AB$ and $BC$ were satisfied within numerical error by appropriate choice of grid dimensions. And the electric potentials within the sphere and the wall are constant.

**Fig. 6.1.** Geometry and boundary conditions for the calculation of electrostatic effects on a charged sphere and a charged wall: CD the wall surface; EF sphere surface. AB and BC natural boundary; boundaries AF and ED, z axis, line of symmetry
6.2.2 Results and Discussion

The Poisson-Boltzmann equation is solved using an adaptive finite element method to obtain the potential distribution. The results are obtained for the case of a single charged sphere at various distances from a single charged planar surface, for constant surface potential conditions.

For the scaled separation distance \( L \), a zero value of \( L \) denotes that the sphere is touching the wall, and positive values of \( L \) mean that the sphere is away from the wall.

The purpose of this section is to provide a basis for comparison with the three-dimensional model presented later on. In addition, it will demonstrate the two-dimensional model and meshing process in more detail.

Figure 6.2 below shows the potential distribution for the case of constant surface potential value of 1 on both the sphere surface and the wall surface, with reduced sphere-wall separation distance (\( L \)) values of 1, 2 and 3. Scaled separation distance is used in the graph; defined by the ratio of the evaluation point distance to sphere to that of the sphere-wall separation distance.

And in a similar manner the results were obtained for the case of constant surface potential value of 2 on sphere surface and wall surface, as can be seen in figure 6.3 which show the results for the case of sphere-wall separation distance values of 1, 2 and 3.
**Fig. 6.2.** Potential values from sphere surface to wall surface for surface potential of 1 on both ($\kappa_1 = 1$)

**Fig. 6.3.** Potential values from sphere surface to wall surface for surface potential of 2 on both ($\kappa_1 = 1$)
In figures 6.4 and 6.5 next, an example of mesh refinement for the case of sphere and a wall is displayed. The first figure shows the coarse mesh, while the second figure shows a refined mesh. In this work, optimal meshes can be obtained after just a few stages, even with fairly coarse initial meshes. In addition, there are regions of high gradients that may need further mesh refinement; this is done automatically in the simulation process [Bowen and Sharif, 1997].

The adaptive process is driven by a global error estimate. Thus, the process terminates when a specified target error has been reached. If the predicted value of the percentage global error is higher than a preset value then the mesh needs to be refined; otherwise the adaptivity process is completed. In this case, a global target error of 0.1% has been chosen.

The meshes shown in figures 6.4 and 6.5 are for the case of a charged spherical next to a charged wall with $\kappa a=1$, $\Psi_w=1$, $\Psi_s=1$ and $L=0.5$. An initial mesh with nine-noded quadrilateral elements (figure 6.4) was produced first. As further refinement was required, the subsequent mesh in figure 6.5 was generated according to the adaptive procedure.
Fig. 6.4. Coarse mesh for the case of a charged spherical particle near a charged wall indicated by the right edge.

Fig. 6.5. Successively refined mesh for the case of a charged spherical particle near a charged wall indicated by the right edge.
Figure 6.6 below, shows the potential field over the mesh area for the case of a wall reduced surface potential=1, sphere reduced surface potential=1 and reduced radius=1, with dimensionless separation distance=0.5.

Fig.6.6. The potential distribution for the case of a charged sphere near a charged wall for $\Psi_w=1$, $\Psi_s=1$ and $\kappa a=1$ case, with $L=0.5$
6.3 Electrostatic Interaction between Two Spheres

6.3.1 Problem Definition

The calculation of electrostatic effects of a chain of identical spherical particles with the special case of two identical spherical particles had a significant role in many fields to estimate multi-body interactions, especially when more complex systems prove difficult to solve.

For the geometry shown above, which represents the above mentioned case taking advantage of the symmetric nature of the problem, \( \Psi = \Psi_s \) on the boundary \( EF \) (which refers to the sphere surface), axisymmetry of the geometry implies that derivatives with respect to the coordinates \( R \) on the lines \( AF, ED \) are assumed to be zero. The natural boundary conditions of the Neumann type on lines \( AB \) and \( BC \) were satisfied within numerical error by appropriate choice of grid dimensions. Constant electric potentials within the two spheres are considered.
6.3.2 Results and Discussion

The normalized Poisson-Boltzmann equation is solved numerically using an adaptive finite element method, to obtain the potential distribution, which is needed to calculate the free energy of interaction and the resulting electrostatic force.

The accuracy of the adaptive finite element solution for the formulae derived in the preceding sections has been tested against existing numerical solutions particularly those of [McCartney and Levine, 1969] (M.L.).

In the present results, the radial distance between the sphere and the confining natural boundary in the radial direction is chosen to be large enough so that the potential or surface charge density on that boundary wall is close to zero to fit with M.L. numerical data.

Figure 6.8 shows the computed dimensionless electrostatic force between two identical charged spheres with reduced surface potential \( \Psi_s = 4 \) and reduced sphere radius \( \kappa a = 10 \), in comparison with M.L. results. The agreement between the two curves is very close.
Fig. 6.8. Comparing present results with those of McCartney and Levine [M.L.] in terms of dimensionless electrostatic force between two identical charged spheres
(reduced surface potential=4, reduced sphere radius=10)

Results for the dimensionless free energy of interaction for the two spheres with the reduced surface potential $\Psi_r=2$ and the reduced sphere radius $\kappa a=5$, are also shown in Figure 6.9, where a similar pattern of the force is observed with M.L. results for similar conditions.
Fig. 6.9. Comparing present results with those of McCartney and Levine [M.L.] in terms of dimensionless free energy of interaction for two identical charged spheres (reduced surface potential=2, reduced sphere radius=5)

The comparison of the two charts shows very good agreement for both electrostatic force and the free energy of interaction.

In the next table, another comparison with the results of the two spherical particles (with surface potential value of 1) from [Bowen and Shairf, 1997] is shown. As it can be seen, the results are very close to each others.
The motive of this section is to validate the model and verify the results by comparing them with previous numerical data, and to provide a comparison case to be used with the results of a chain of spheres inside a chain of rings which will be the main focus of this chapter. Also, it will serve as another validation case for the three-dimensional code.
6.4 Electrostatic Interaction of Confined and Unbounded Chains of Spheres

6.4.1 Problem Definition

In this section, the calculation of electrostatic effects of chain of identical spherical particles is presented. It can be considered as extension to the previous case, but it has its own practical implications in M.B. colloidal systems.

Taking full advantage of the symmetry allows simple geometry to be used, which comprises a single charged sphere (representing a particle) confined in a charged tube (representing a pore), or unconfined.

For the geometry shown above, which represents the case of a chain of spheres making use of the symmetry in this problem, surface charge density $\sigma_s=\partial \psi / \partial N$ on
the boundary \( EF \) (which refers to the sphere surface), axisymmetry of the geometry implies that derivatives with respect to the coordinates \( R \) on the lines \( AF, ED \) are assumed to be zero. The natural boundary conditions of the Neumann type on line \( BC \) were satisfied within numerical error by appropriate choice of grid dimensions. And the electric potentials within all the spheres are constant.

### 6.4.2 Results and Discussion

Figure 6.11 below shows the computed dimensionless force between any two spheres in a long and unbounded chain of identical charged spheres with reduced surface charge density \( \sigma_s = 2 \) and reduced sphere radius \( m = l \), while figure 6.12 use the surface potential boundary condition \( \Psi_s = 2 \), both in comparison with those of [Sharif et al., 2003] for the unconfined case.

![Graph showing dimensionless force versus dimensionless surface-surface distance](image)

**Fig.6.11.** Comparing present results with those of Sharif et al. [S.A.M.W.] in terms of dimensionless electrostatic force between any two spheres in a long chain of identical charged spheres (reduced surface charge density=2, reduced sphere radius=1)
Chapter 6

Fig. 6.12. Comparing present results with those of Sharif et al. [S.A.M.W.] in terms of dimensionless electrostatic force between any two spheres in a long chain of identical charged spheres (reduced surface potential=2, reduced sphere radius=1)

As it can be observed from the figure, the two sets of data have a very close agreement. Next Figure 6.13 shows the effect of wall confinement on the electrostatic force between any two spheres in a long chain of spheres confined (bounded by a tube) with different values of sphere radius to tube radius ratio $\lambda$. Comparing the curves, it can be noted that the electrostatic force for confined spheres is less than that for less confined (smaller $\lambda$) or isolated spheres with the same surface potential which agree with the reference work.
Fig. 6.13. Comparing results for different values of $\lambda$ on the electrostatic force
(reduced sphere potential=2, reduced tube potential=2)

The results demonstrated in this section serve as another validation case for the 2D model by comparing its results with existing numerical data. It also illustrates the concept of a particle’s confinement and its effect on electrostatic force between the spheres which would be of interest in subsequent cases.
6.5 Electrostatic Interaction of a Chain of Spheres inside a Chain of Rings

6.5.1 Problem Definition

In this section, the quantification of electrostatic effects of a chain of identical spherical particles inside a chain of ring-like object has been considered; the ‘ring’ cross section circle is of the same radius as that of the spherical particles in the centre. An assumption is made here that the potential field is symmetric between the sphere and the ring around the mid-distance between them. This geometry setting is used to provide approximate quantification of electrostatic behaviour of an array of spheres at the lower cost of two-dimensional simulation. For better emulation of the array geometry, the separation distance between each sphere and the surrounding ring is chosen to equate the separation distance between the spherical particles themselves.

Figure 6.14 shows the system we approximate; that of a chain of identical spherical particles inside a chain of rings of similar cross section radius to that of the spheres.

![Fig.6.14. Chain of spheres inside chain of rings](image-url)
This system geometry (Figure 6.14) is of a symmetrical nature making it possible to use simple geometry to represent the same geometry. Furthermore, taking into account the axial symmetry around the line passing through the centres of the spherical particles, and taking into account the symmetry between adjacent spheres and rings, this geometry can be reduced to that of figure 6.15, which can be reasonably assumed to represent the whole system.

Fig. 6.15. 2D solution domain of our system

For the geometry shown above, we define the potential $\Psi_s$ and the potential gradient in the outward normal direction $\partial \Psi / \partial N$ at the boundary $\Gamma$ in the case of constant surface potential. $N = \kappa n$ is the dimensionless outward normal direction from the boundary $\Gamma$. The length of the lines $AF$ and $ED$ is half the distance between adjacent spherical surfaces, which is equal to the line normal on both sphere surface $FE$ and $BC$ (the midplane between the sphere and the ring’s circle on the 2D plane), so the lines $AB$ and $CD$ can be considered as the mid-planes with the adjacent spheres. Axisymmetry of the geometry implies that derivatives with respect to the coordinates $R$ on the lines $AF$, $FE$, $ED$, and derivatives with respect to the coordinates $Z$ on the lines $AB$, $DC$ are both assumed to be zero.
6.5.2 Results and Discussion

The effect of many-body electrostatic interactions has been quantified for a system of chain of spheres inside chain of rings with constant surface potential and constant surface charge density conditions. Results are expressed in terms of the dimensionless electrostatic force on charged spheres at various distances from each other.

![Graph showing results comparison between different geometries.](image)

*Fig. 6.16. Results comparison between number of systems (reduced surface charge density=1, reduced sphere radius=1)*

The electrostatic force between any two spheres in our chain of spheres inside chain of rings system, is calculated for a dimensionless sphere radius $\kappa a = 1.0$. Figure 6.16 shows results obtained for different geometries for reduced surface charge density = 1.0.
Results have then been obtained for different reduced sphere potentials 1.0 and 2.0 for the same set of geometries. With $\Psi_s = 1.0$, figure 6.17 compares the results of a chain of spheres inside a chain of rings arrangement with the results obtained for systems of two isolated spheres, and two spheres in a charged tube ($\Psi_{tube} = 1.0$) with tube confinement set to equate the separation distance at evaluation points to emulate array arrangement. Figure 6.18 shows similar comparison with $\Psi_s = 2.0$ and $\Psi_{tube} = 2.0$.

Fig. 6.17. Dimensionless E.F. for different geometries (reduced surface potential=1, reduced sphere radius=1)
It can be noted that at relatively larger distances (>1.1 in figure), the electrostatic force is higher for the case of the chains system than that of two spheres, which predicts that the dispersed system would be more stable than the two isolated spheres system.

The results of the chains system demonstrate a different behaviour than those of the two isolated spheres when the separation distance between particles becomes small enough, as the E.F. will start falling below a ‘peak’ E.F. value. This behaviour can be attributed to a ‘cancelling’ effect that results from getting the spheres at different axes to minimal separation distances, which affects the electrical double layer of the spheres involved, and gives rise to effective force components in different directions; resulting in reduction of the electrostatic force between adjacent spheres.
This can be confirmed also with the case of two charged spheres in a charged tube with varying confinement, which shows a similar behaviour albeit with smaller force values due to more effective ‘charge confinement’ for the spheres.

This behaviour of the chains system is further demonstrated in Figures 6.19 and 6.20, with reduced sphere potential values $\Psi_s = 1$ and 2 respectively, for dimensionless sphere radius values $\alpha = 0.1$, 0.5 and 1.

**Fig.6.19.** Electrostatic Force results for the chains system with dimensionless radius values 0.1, 0.5 and 1.0 (reduced surface potential=1)
In all of these figures, we can notice a maximum value for the electrostatic force on the curve, with falling values next to it. The peaks of the repulsive electrostatic force potential observed in those figures move to smaller surface separations as the sphere radius is allowed to increase. This can be attributed to the fact that the thickness of the electrical double-layer will shrink closer to the particle as normalized sphere radius increases, meaning either sphere radius increase or electrolyte concentration increases [Hunter, 2001].

To conclude this chapter, the effect of the many-body electrostatic interactions has been quantified for multi-body systems of spherical particles inside chain rings with constant surface potential and constant surface charge density conditions. Results are expressed in terms of dimensionless electrostatic force between each pair of two charged spheres.

Calculations based on the dimensionless separation distance between a pair of charged spheres in isolation confirm an exponential decay of the repulsive electrostatic force as the surface to surface separation distance is increased. In contrast, calculations based on a chain of interacting spheres inside a chain of
rings reveal considerable reduction in the magnitude of the repulsive electrostatic force at small-enough separation distances. The latter results are explained by considering the directional 'cancellation' effects of the electrical double layer between adjacent spheres within the system. This notion will be addressed again in a subsequent chapter, to measure how it is relevant to the actual behavior of an array of spherical particles system.
Chapter 7

Three-Dimensional Electrostatic Interactions Models

7.1 Introduction

This chapter presents and discusses a number of three-dimensional cases; particularly: (i) of an isolated spherical particle; (ii) a spherical particle and a wall; (iii) two interacting identical spherical particles; (iv) an array of spheres; and (v) two spheres approaching a wall.

Calculations have been carried out for a range of different values of parameters: sphere surface potential/sphere charge, sphere radius/tube radius ratio, sphere/wall potential.

The first three cases serve to an extent as validation cases for the three-dimensional code. The last two cases, that of an array of spheres and that of two spheres approaching a wall, are of more interest and will be the focus of the chapter, as they are more accounting for multi-body effects in multi-body systems that can be found in practice.

Occasionally, the mesh generating software would give mesh that results in null determinants due coinciding nodes coordinates, in these occasions, slight coordinates adjustments were used to avoid such situation.
7.2 3D Electrostatic Results of an Isolated Charged Sphere

7.5.2 Problem Definition

The quantification of electrostatic effects of a single charged spherical particle with different sphere potential values and for various sphere radii is considered first in this chapter, mainly for the purpose of verifying the 3D model.

Fig. 7.1. Solution domain of an isolated charged spherical particle: I sphere surface (half sphere); ABCD, EFGH, ADHE, BCGF and CDHG natural boundary planes; ABFE symmetry plane boundary
For the geometry shown above, which represents an isolated charged sphere; by taking advantage of the symmetry in the problem, only half of the problem is considered with $ABFE$ representing the symmetry plane. The natural boundary planes $ABCD, EFGH, ADHE, BCGF$ and $CDHG$ are taken far enough from the sphere. Constant electric potentials within the two spheres are considered with $\Psi = \Psi_s$ on the boundary $I$ (which refers to the sphere surface).

### 7.5.2 Results and Discussion

The Poisson-Boltzmann equation is solved using a finite element method to obtain the potential distribution. Results are expressed in terms of the dimensionless total free energy and the electrostatic force for different surface properties and system dimensions.

Figure 7.2 shows a comparison between the two dimensional model and the three dimensional model for the case of an isolated charged sphere. The results are expressed in term of total free energy for various normalized particle radius $ka$ values, with constant sphere surface potential value of 1.
Fig. 7.2. Comparing results for different values of reduced sphere radius against the dimensionless total free energy (sphere potential=1)

In similar manner, figure 7.3 shows a comparison between the two dimensional model and the three dimensional model for the case of an isolated charged sphere, for different reduced sphere potentials this time, with particle radius $\kappa a$ value of 1. As in previous figure, the results are expressed in terms of total free energy.

Fig. 7.3. Comparing results for different values of reduced sphere potential against the dimensionless total free energy (sphere radius=1)
Both figures presented above show a very close agreement between the two models for different sphere potential values, and for various radii for the spherical particle.

Figures 7.4, 7.5 and 7.6 below, show comparison between the 2D model and the 3D model with regard to the potential distribution away from an isolated spherical particle with sphere radius $ktt$ value of 1, and for surface potential values of 1, 2 and 3 respectively. Very close agreement between the two models can be seen in those three figures.

**Fig.7.4.** Electric potential at different distance values to spheres surface (sphere radius=1, sphere potential = 1)
Fig. 7.5. Electric potential at different distance values to spheres surface (sphere radius = 1, sphere potential = 2)

Fig. 7.6. Electric potential at different distance values to spheres surface (sphere radius = 1, sphere potential = 3)
7.3 3D Electrostatic Interaction of a Sphere and a Wall

7.3.1 Problem Definition

In this section, the calculation of electrostatic effects of a single charged spherical particle at various distances from a charged wall is presented. Figure 7.7 illustrates the solution domain of this case, and by taking advantage of the symmetry, only half of the solution domain is considered.

Fig. 7.7a. Solution domain of a spherical particle approaching a wall: I sphere surface (half sphere); BCGF wall surface; ABCD, EFGH, ADHE and CDHG natural boundary planes; ABFE symmetry plane boundary
Fig. 7.7b. Cross section of the solution domain of a spherical particle approaching a wall: I sphere circle; BF represents wall plane, AB, FE, EA represents the natural boundary planes

For the figure shown above which defines the main geometry of interest in this chapter; ABFE is a plane of symmetry such that the problem domain is reduced by half. ABCD, EFGH, ADHE and CDHG are the natural boundary planes. Distances between the sphere and the natural boundary planes are taken to be large enough so that the potential on those boundary walls is close to zero. BCGF is the charged wall surface. Constant electric potentials within the two spheres and on the wall are considered with $\Psi = \Psi_s$ on the boundary I (which refers to the sphere surface), and $\Psi = \Psi_w$ on the wall surface.

The Poisson-Boltzmann equation is solved using finite element methods to obtain the potential distribution.

The results were obtained for the case of a single charged sphere at various distances from a single charged planar surface, for constant surface potential
conditions. For the scaled separation distance $L$, a zero value of $L$ denotes that the sphere is touching the wall, and positive values of $L$ mean that the sphere is away from the wall.

### 7.3.2 Results and Discussion

Taking full advantage of the symmetry allows a smaller geometry to be used, which allows a reduction in the computational requirements.

Figure 7.8 shows the potential distribution comparison between the 2D model and the 3D model for the case of constant surface potential of 1 on both the sphere surface and the wall surface, with sphere-wall separation distance ($L$) values of 1, 2 and 3. Scaled separation distance is used in this graph; defined by the ratio of the evaluation point distance to sphere to that of the sphere-wall separation distance.

![Graph showing potential distribution comparison between 2D and 3D models](image)

**Fig.7.8.** Potential values from sphere surface to wall surface for surface potential of 1 on both (sphere radius=1)
The comparison was redone for the case of constant surface potential value of 2 on sphere surface and wall surface, as can be seen in figure 7.9 which compares the results for the case of sphere-wall separation distance values of 1, 2 and 3 for both the 2D and 3D models.

![Figure 7.9](image)

**Fig. 7.9.** Potential values from sphere surface to wall surface for surface potential of 2 on both (sphere radius = 1)

As it can be observed from previous figures, the two sets of data for the 2D model and 3D model of the case of a charged sphere next to a charged wall demonstrate a very close agreement.
In Figure 7.10 a 3D mesh example is illustrated. The figure shows the mesh for the case of a spherical particle near a wall, where the sphere half is visible on the top symmetry plane, and the wall is farthest plane in y-direction, with sphere-wall separation distance value of 2 and sphere radius 1.

Fig. 7.10. 3D mesh example for the case of a spherical particle with radius value of 1 approaching a wall with sphere-wall separation value of 2
Next, Figure 7.11 shows the potential field over the mesh area demonstrated in the previous figure, particularly on the symmetry plane (the top plane). That is with wall reduced surface potential=1, sphere reduced surface potential=1, sphere-wall separation distance=1 and sphere radius=1.

Fig. 7.11. The potential distribution for the case of a sphere near a charged wall for $\Psi_w=1$, $\Psi_s=1$ and $\kappa a=1$ case, with $L=2$
The accuracy of the finite element solution for the three dimensional case has been tested against the established model of two spherical charged particles in two dimensions presented in a previous chapter.

In the present results, the distance between the sphere and the natural boundary planes is chosen to be large enough so that the potential on those boundary walls is close to zero.

Figure 7.13 shows the computed dimensionless electrostatic force between two identical charged spheres with reduced surface potential $\Psi_s = 1$ and reduced sphere radius $\kappa a = 1$. The agreement between the two curves is very close overall.

**Fig.7.13.** Comparing present results with those of the 2D model in terms of dimensionless electrostatic force between two identical charged spheres (reduced surface potential=1, reduced sphere radius=1)
Results for the dimensionless free energy of interaction for the two spheres with the reduced surface potential $\Psi_r = 1$ and the reduced sphere radius $ka = 1$, are also shown in Figure 7.14, where a similar pattern of the force is observed with 2D model results for similar conditions.

**Fig. 7.14.** Comparing present results with those of 2D model in terms of dimensionless free energy of interaction for two identical charged spheres (reduced surface potential=1, reduced sphere radius=1)

Figures 7.15 and 7.16 below show a similar comparison with sphere potential value of 2. The first figure shows the results in terms of electrostatic force, while the second figure shows them in terms of free energy of interaction.
**Fig. 7.15.** Comparing present results with those of the 2D model in terms of dimensionless electrostatic force between two identical charged spheres (reduced surface potential=2, reduced sphere radius=1).

**Fig. 7.16.** Comparing present results with those of 2D model in terms of dimensionless free energy of interaction for two identical charged spheres (reduced surface potential=2, reduced sphere radius=1).

The comparison of the previous charts again shows a close agreement for both electrostatic force and the free energy of interaction between the two models.
7.5  3D Electrostatic Results of an Array of Spheres

7.5.1  Problem Definition

The quantification of electrostatic effects of an array of identical spherical particles at various distances from each other has practical implications as it is more representative of concentrated colloidal systems.

**Fig. 7.17. Solution domain of an isolated charged spherical particle: I sphere surface (half sphere); ABCD, EFGH, ADHE, BCGF and CDHG are midplanes of symmetry; ABFE symmetry plane boundary**
For the geometry shown above, which represents array of spheres system; by taking advantage of the symmetry in the problem, only half of the problem is considered with $ABFE$ representing the symmetry plane. The planes $ABCD$, $EFGH$, $ADHE$, $BCGF$ and $CDHG$ are midplanes of symmetry between the central sphere and each of the surrounding spheres and with equal separation distance to the central sphere. Constant electric potentials for the spheres are considered with $\Psi = \Psi_s$ on the boundary I (which refers to the sphere surface).

### 7.5.2 Results and Discussion

The Poisson-Boltzmann equation is solved using finite element methods to obtain the potential distribution. Results are expressed in terms of the dimensionless total free energy and the electrostatic force for different surface properties and system dimensions.

Results have been obtained for number of systems, with different reduced sphere potentials. With $\Psi_s = 1.0$, figure 7.18 compares the results of the array of spheres with the results obtained for systems of two isolated spheres, and that of a chain of spheres inside chain of rings from an earlier chapter. Figure 7.19 shows similar comparison with $\Psi_s = 2.0$. 
**Fig. 7.18.** Comparison of results with different systems (reduced surface potential=1, reduced sphere radius=1)

**Fig. 7.19.** Comparison of results with different systems (reduced surface potential=2 reduced sphere radius=1)
As seen for the case of spheres inside rings chains, it can be noted that at relatively larger distances, the electrostatic force is higher for the case of the array than that of two spheres, which means that the dispersed system would be more stable than what the two isolated sphere results can predict.

The results of the arrays of spheres system (similar to those of the chains system) demonstrate behaviour different from those of the two adjacent spheres in isolation: When the separation distance between particles sufficiently reduced (i.e. \(< 0.5\) sphere radius), then the repulsive electrostatic force is forced to fall below the ‘peak’ electrostatic force value. This behaviour can be attributed to a ‘cancelling’ effect that results from getting the spheres at three axes to minimal separation distances, which affects the electrical double layer of the spheres involved, and give rise to effective force components in different directions; resulting in reduction of the electrostatic force between adjacent spheres.

This also confirms the validity of the chains model presented in earlier chapter to estimate the behaviour of an array of spheres system, as both systems curves show a similar trend, albeit with smaller force values in the case of the chains system due to more effective ‘charge confinement’ since the ‘central’ sphere is surrounded by a ‘continuous’ charged ring.

This behaviour of the array of spheres system is further demonstrated in figures 7.20 and 7.21, with a reduced sphere potential values \(\psi = 1\) and 2 respectively, with dimensionless sphere radius values \(xa = 0.1, 0.5\) and 1.
**Fig. 7.20.** Electrostatic force results between array of spheres for dimensionless radius values 0.1, 0.5 and 1.0 (reduced surface potential=1)

**Fig. 7.21.** Electrostatic force results between array of spheres for dimensionless radius values 0.1, 0.5 and 1.0 (reduced surface potential=2)
Same as in the case of the chains system, we can notice a maximum value for the electrostatic force on the curve, with falling values next to it. The peak of the repulsive electrostatic force potential is observed in figures 7.20 and 7.21 to move to smaller surface separations as the sphere radius is allowed to increase. This can be attributed to the fact that thickness of the electrical double-layer will shrink closer to the particle as normalized sphere radius increases when electrolyte concentration increases [Hunter, 2001].

The effect of the many-body electrostatic interactions has been quantified for multi-body system of array of spheres with constant surface potential. Results are expressed in terms of dimensionless electrostatic force between each pair of charged spheres. The results obtained demonstrate a reduction in the repulsive force in arrays of interacting spheres in certain critical packing conditions when the separation distance between them becomes small enough (less than half the sphere radius). This effect can be explained by considering the directional 'cancellation' effects of the electrical double layer between adjacent spheres placed in certain orientations, which results in reduction of the electrostatic force between those adjacent spheres.

The strength and stability of charged sphere arrays achieved at critical packing configurations is a useful design concept which can be used to generate assembly structures that will 'hold together' more easily and will therefore allow bulk movement without significant distortion as in harvesting of nano-particles form sol-gel solutions [Gundogdu et al 2006] or will exhibit enhanced 'tensile strength' of a deformable matrix such as in a liquid separation membrane material [Giancoli, 2000]. It may also be possible to generate other process and product engineering design applications that will benefit from the concepts developed here.
7.6 Electrostatic Interaction of Two Spheres and a Wall

7.6.1 Problem Definition

The first three sections presented in this chapter serve mainly as validation cases for the three-dimensional code presented here; that of two spherical charged particles approaching a charged wall.

The quantification of electrostatic effects of two identical spherical particles at various distances from each other and from a wall has practical implications as it is more representative of some real concentrated colloidal systems in practice with its complex geometries.

Figure 7.22 below illustrates the solution domain of our problem; taking advantage of the symmetry in this problem, only half of the solution domain is considered as it should be enough to describe and model the problem under consideration.
Fig. 7.22a. Solution domain of two interacting identical spherical particles: I sphere surface (half); ABCD midplane of symmetry; BCGF wall surface. EFGH, ADHE and CDHG natural boundary planes; ABFE symmetry plane boundary.

Fig. 7.7b. Cross section of the solution domain of a spherical particle approaching a wall: I sphere circle; AB represents midplane of symmetry, BF represents wall plane, FE, EA represents the natural boundary planes.
For the figure shown above which defines the main geometry of interest in this chapter; $ABFE$ is a plane of symmetry such that the problem domain is reduced by half. $EFGH$, $ADHE$ and $CDHG$ are the natural boundary planes. Distance between the sphere and the natural boundary planes is chosen to be large enough so that the potential on those boundary walls is close to zero. $DABC$ is the midplane of symmetry between the two spherical particles. $BCGF$ is the charged wall surface. Constant electric potentials within the two spheres and on the wall are considered with $\Psi = \Psi_s$ on the boundary $I$ (which refers to the sphere surface), and $\Psi = \Psi_w$ on the wall surface.

### 7.6.2 Results and Discussion

The effect of many-body electrostatic interactions has been quantified for a system of two spherical charged particles near a charged wall with constant surface potential on the spheres and the wall. Results are expressed in terms of dimensionless electrostatic force on the charged spheres at various distances from each other and from the wall.

The electrostatic force between the spheres, is calculated for a dimensionless sphere radius $\kappa a = 1.0$. Results have been obtained first for a reduced sphere potential $\Psi_s = 1.0$ as can be seen in figures 7.23 - 7.25 which shows the results obtained for a wall potential ($\Psi_w$) values 1, 3 and 5, respectively, with varying spheres-wall separation distances.

In figure 7.23 below, for a sphere potential value of 1.0, dimensionless electric force between the two spheres are calculated and presented versus the separation distance between them ($D_s$), where the reduced distance to the wall ($D_w$) values used in each graph are 0.2, 0.5, 1.0 and 2.0. Similarly, for figures 7.24 and 7.25
where the reduced wall potential values are 3.0 and 5.0 respectively (In figure 7.25, $D_w$ value of 0.3 is added for better presentation).

Fig. 7.23. Dimensionless electric force between two charged spheres near a charged wall with respect to separation distance between them (reduced sphere potential=1, reduced wall potential=1)

Fig. 7.24. Dimensionless electric force between two charged spheres near a charged wall with respect to separation distance between them (reduced sphere potential=1, reduced wall potential=3)
Fig. 7.25. Dimensionless electric force between two charged spheres near a charged wall with respect to separation distance between them (reduced sphere potential=1, reduced wall potential=5)

In figures 7.26, 7.27 and 7.28 next, the illustrated results were obtained for reduced sphere surface potential ($\psi_0$) value of 2.0, for wall potential ($\psi_w$) values of 2, 4 and 6 respectively. The figures present a similar trend to that of earlier ones.
Fig. 7.26. Dimensionless electric force between two charged spheres near a charged wall with respect to separation distance between them (reduced sphere potential=2, reduced wall potential=2)

Fig. 7.27. Dimensionless electric force between two charged spheres near a charged wall with respect to separation distance between them (reduced sphere potential=2, reduced wall potential=4)
The previous figures show very interesting results; in systems with the wall potential sufficiently higher than that of the spheres, and with spheres close enough to the wall, an electrostatic attractive force can be experienced between the spherical particles. This attractive force can increase in value as the spheres get closer to the wall.

This phenomenon can be attributed to the multi-body nature of the problem. Furthermore, this long range attraction can be explained by the redistribution of the static electric double layer of ions and counter-ions in solution around the spheres, caused by the presence of the wall. With the spheres close to each other, they experience an electrostatic interaction in the region between them. In addition, each sphere experiences another electrostatic interaction with the wall, in particular, on the other side away from the adjacent sphere. With relatively higher
wall potential, this wall-sphere interaction for both spheres would push the spheres closer to each other, causing them to show an attractive behavior.

On even smaller separation distances between the spheres, however, the wall-sphere repulsive force will not be sufficient to overcome the repulsive force between the spheres as they get very close to each other, which will cause them to show a repulsive behavior over again.

Figures 7.29 and 7.30 below show the potential distribution for a repulsion scenario and an attraction one respectively. Also, appendix D shows some potential gradient figures illustrating the two scenarios.

The above mentioned behavior agrees with experimentally observed phenomena of long range electrostatic attractive force [Larsen and Grier 1996, Crocker and Grier 1996] that presented an unresolved issue within the scientific community due to the assumption that current theories of colloidal system were unable to explain these phenomena and that a substantial revision to existing concepts of colloidal interactions is needed to be able to [Larsen and Grier 1997].

These results can also help explain observations of stable multi-particle voids in colloidal fluids and crystals, phase separation between fluid phases of different densities, and long-lived, metastable colloidal crystallites in dilute suspensions [Crocker and Grier 1996].
**Fig. 7.29.** The potential distribution for the case of two charged spheres approaching a charged wall for $\Psi_w = 5$, $\Psi_s = 1$ and $a = 1$ case, with $D_s = 0.5$, $D_w = 2.0$ (repulsive behaviour)

**Fig. 7.30.** The potential distribution for the case of two charged spheres approaching a charged wall for $\Psi_w = 5$, $\Psi_s = 1$ and $a = 1$ case, with $D_s = 0.5$, $D_w = 0.2$ (attractive behaviour)
Chapter 8

Conclusions and Future Work

8.1 Conclusions

Electrostatic interactions between charged surfaces have been modelled based on
the Boltzmann theory using two and three dimensional finite element models. The
normalized Poisson-Boltzmann equation Eq.[5.6] is solved numerically to obtain
the potential distribution. An adaptive finite element method combined with error
estimation and the Newton sequence technique is used for the non-linear terms.
Obtained potential distributions were used to calculate the free energy of
interaction using Eq.[5.14]. The electrostatic force was obtained directly from
Eq.[5.20] or by differentiating the free energy of interaction with respect to the
separation distance from Eq.[5.16]. Results are shown in terms of dimensionless
free energy of interaction and dimensionless repulsive force.

Computed results for electrostatic effects have been analyzed in terms of the free
energy of interaction and repulsive force on a single and multiple charged
sphere(s) at various distances from other charged particle/wall surfaces for
constant surface potential and/or surface charge density conditions. The variables
of interest are the normalized particle radius \( \kappa a \), the size ratio \( \lambda \), the scaled
separation distance \( L \), with the reduced surface potential and reduced surface
charge density for the different particles and geometries described in the previous
sections.
The model proved to be effective in quantifying the electrostatic interactions of different systems. Comparison with previous numerical work has shown very good agreement which demonstrates the validity of the present numerical technique in analyzing electrostatic interactions and allowed the extension to model other colloidal systems.

More complex geometries with better representation of real system were applied in this study; this includes the cases of arrays of spheres and that of two spheres approaching a wall, which depict the multi-body interactions more accurately than existing models, and explain some inconsistencies/shortages the PBE theory were thought to have previously.

8.2 Future work

The difficulty and inaccuracy of representing some important industrial applications with simplified geometries suggest the need for more complex geometries that accurately represent real systems.

More complex geometries will be modelled using a 3D code in order to quantify other multi-body electrostatic interactions in systems such as membrane and multi-body colloidal systems. Examples are the case of two spheres approaching a curved wall and that of arrays of spheres with complex or asymmetric arrangements. The model will be valuable in analyzing the behaviour of multi-body interaction in these systems.
The results obtained for the case of array of spheres could be exploited in more industrial and practical sense; this may open the door for a wide range of applications and may influence better techniques to be implemented in different fields.

Other work can include the development of a user friendly interface program for the 2D and 3D codes, with integrated tools to ensure simplicity and practicality for users, such as data plotting and mesh viewing.
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Appendix A: Boltzmann distribution

The Boltzmann distribution gives the most probable distribution of a system of particles among the various energy states, i.e., if we have a system of \( N \) particles \((N=\Sigma n_i)\), it gives the most probable distribution of finding \( n_1 \) particles with energy \( u_1 \), \( n_2 \) particles with energy \( u_2 \) and so on. The assumption made while deriving this expression is that the probability of finding \( n_i \) particles with energy \( u_i \) \((i=1, 2, 3...)\) is respectively proportional to the number of possible ways of distributing them so. We use \( W \) to denote the number of ways of distributing \( n_i \) particles with energy \( u_i \), respectively as given by equation [A1], where \( g_i \) is the number of states with energy \( u_i \). Note that within any given energy state the permutations are immaterial.

\[
W = \frac{N!}{n_1! n_2! \cdots} g_1^{n_1} g_2^{n_2} \ldots \tag{A1}
\]

To maximize \( W \), we can maximize \( \ln W = \ln N! - \sum_i \ln n_i! + \sum_i \ln g_i \). Using Stirling’s formula: for large \( n_i \), \( \ln N! \approx N \ln N - N \) and using the relation \( N = \sum_i n_i \), we get \( \ln W = N \ln N - \sum_i n_i \ln n_i + \sum_i n_i \ln g_i \). For \( \ln W \) to be maximized the variation \( \delta (\ln W) = 0 \) (again this is in the discrete sense using difference calculus). Using the conservation of total energy, \( \delta U = \sum_i \delta n_i u_i \), we get the well known form of the Boltzmann distribution:

\[
n_i = n_\infty \exp \left( -\frac{u_i}{k_B T} \right) \quad \forall i \in N \tag{A2}
\]
Here, $n_m$ is the mean distribution at far-field and $k_B$ is the Boltzmann constant and $T$ is the absolute temperature of the system. The constants $n_m$ and $\frac{1}{k_B T}$ were chosen empirically.
Appendix B: Additional figures for two spheres and a wall

Many runs and tests were performed during the process of this study, some were partially correct, some needed slight adjustments, some were completely invalid and a whole new set of simulations were needed. In this appendix few figures for the last case of this thesis (two spheres approaching a wall) are presented, these figures weren’t included in the main text for the sole reason they would be similar to the used results. However, since they were a complete set of results that may be of some interest and took a considerable time to finish correctly, this appendix was added. $D_w$ indicate the sphere-wall separation distance here.

![Dimensionless electric force between two charged spheres near a charged wall with respect to separation distance between them (reduced sphere potential=0.5, reduced wall potential=1)](image)

**Fig.A2.1.** Dimensionless electric force between two charged spheres near a charged wall with respect to separation distance between them (reduced sphere potential=0.5, reduced wall potential=1)
**Fig. A2.2.** Dimensionless electric force between two charged spheres near a charged wall with respect to separation distance between them (reduced sphere potential=0.5, reduced wall potential=2)

**Fig. A2.3.** Dimensionless electric force between two charged spheres near a charged wall with respect to separation distance between them (reduced sphere potential=1.5, reduced wall potential=3)
Fig.A2.4. Dimensionless electric force between two charged spheres near a charged wall with respect to separation distance between them (reduced sphere potential=1.5, reduced wall potential=5)
Appendix C: Mesh figures and potential fields

Throughout the thesis different geometries and mesh figures were used, those geometries and figures went through many changes until it reached its final state which we used to perform the calculations. In this appendix, selected mesh figures and potential fields for some cases tackled here is shown.

Figures A3.1, A3.2 show the mesh for the case of two isolated spheres with separation distance value of 0.5, surface potential value of 1 and sphere radius value of 1, for coarse and refined mesh respectively.

![Figure A3.1. Coarse mesh for the case of two charged spherical particles](image)

**Fig.A3.1. Coarse mesh for the case of two charged spherical particles**
**Fig. A3.2.** Adaptive refined mesh for the case of two charged spherical particles

Figure A3.3 next shows the potential field for the abovementioned case.

**Fig. A3.3.** The potential distribution for the case of two charged spheres with \( \Psi_z = 1 \) and \( \kappa \alpha = 1 \) case, with \( L = 0.5 \)
In similar pattern, figures A3.4-A3.6 show the mesh figures and potential distribution for the case of chain of spheres inside a tube. Followed by figures A3.7-A3.9, that illustrate them for the cases of chain of spheres inside chain of rings with comparable conditions.

**Fig.A3.4. Coarse mesh for the case of chain of spheres inside a tube**
Fig.A3.5. Adaptive refined mesh for the case of chain of spheres inside a tube
Fig.A3.6. The potential distribution for the case of chain of spheres inside a tube with $\Psi_a=1$, $\Psi_l=1$ and $\kappa\alpha=1$ case, with $L=0.5$.

Fig.A3.7. Coarse mesh for the case of chain of spheres inside chain of rings.
Fig. A3.8. Adaptive refined mesh for the case of chain of spheres inside chain of rings.

Fig. A3.9. The potential distribution for the case of chain of spheres inside chain of rings with $\Psi_s=1$ and $\kappa a=1$ case, with $L=0.5$. 
Similarly, figures A3.10-A3.12 show this for the case of chain of spheres inside chain or rings where the rings are located at the midplanes between each two spheres. This case was not included in the thesis but it has a similar behavior to that of normal chain of spheres inside chain of rings.

Fig.A3.10. Coarse mesh for the case of alternative chain of spheres inside chain of rings system
Fig.A3.11. Adaptive refined mesh for the case of alternative chain of spheres inside chain of rings system.

Fig.A3.12. The potential distribution for the case of alternative chain of spheres inside chain of rings system with $\Psi_z=1$ and $\kappa=1$ case, with $L=0.5$. 
All figures in this appendix so far are for the 2D model cases. Next, we’ll show the potential distribution for selected 3D model cases, as no mesh refinement process is involved here.

Figure A3.13 show the potential distribution over a cross-section of the geometry, for the case of two spheres at separation distance value of 2.

Fig.A3.13. The potential distribution for the case of two charged spheres with $\Psi = 1$ and $\kappa=1$ case, with $L=1$

Similarly, figures A3.14 and A3.15 show the potential distribution for the cases of array of spheres and two spheres approaching a wall respectively.
Fig.A3.14. The potential distribution for the case of an array of spheres with
\( \Psi = 1 \) and \( \kappa a = 1 \) case, with \( L = 1 \)
Fig.A3.15. The potential distribution for the case of two spheres approaching a wall with $\Psi_w = 1$, $\Psi_z = 1$ and $\alpha = 1$ case, with $L_{\text{spheres}} = 1$ and $L_{\text{sphere-wall}} = 1.5$
Appendix D: Two spheres and a wall potential gradient

To further confirm the results of two spheres approaching a wall in 7.6. Potential gradients were illustrated for the cases of both attraction and repulsion. The figures confirm the findings; however, they are either not clear or not presentable enough to be included in the main text.

For the case of the repulsive behavior, figure A4.1, below. The potential gradient vector field for one sphere is shown in figure A4.2. A potential gradient on the x-axis direction only is presented in figure A4.3.

![Potential distribution for two charged spheres approaching a wall](image)

**Fig.A4.1.** The potential distribution for the case of two charged spheres approaching a charged wall for $\Psi_w=5$, $\Psi_s=1$ and $k_w=1$ case, with $D_s=0.5$, $D_w=2.0$ (repulsive behaviour)
Fig. A4.2. The potential gradient vector field for the repulsion case, where the right end represents the midplane
Fig. A4.3. The potential gradient in x-axis direction for the repulsion case, where the right edge represents the midplane

Similarly, for the case of the attractive behavior, figure A4.4, below. The potential gradient vector field for one sphere is shown in figure A4.5. A potential gradient on the x-axis direction only is presented in figure A4.6.
Fig. A4.4. The potential distribution for the case of two charged spheres approaching a charged wall for $\Psi_w = 5$, $\Psi_z = 1$ and $\kappa a = 1$ case, with $D_z = 0.5$, $D_w = 0.2$ (attractive behaviour)
Fig.A4.5. The potential gradient vector field for the attraction case, where the top and the right ends represent the wall and midplane respectively.
Fig.A4.6. The potential gradient in x-axis direction for the attraction case, where the top and the right ends represent the wall and midplane respectively.
Appendix E: Program flow-chart

The general flow-chart of the program can be seen in figure A5.1.

Fig.A5.1. The program general flow-chart