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A Mathematical Model for Colloidal Aggregation

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A Mathematical Model for Colloidal Aggregation

by

Colleen S. O’Brien

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering
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DEDICATION

I would like to dedicate this work to my fiancé, Brian. His encouragement, patience, and love have enabled me to pursue my passion, and continue to strive for excellence in all areas of my life.
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I would like to use this opportunity to thank everybody without whose help this work would have not been possible.

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3.8 Summary

CHAPTER 4: EXPERIMENTS CONDUCTED BY MATHEMATICAL MODEL 94

4.1 Introduction 94
4.2 The Effect of Discretizing Parameters on the Model 94
4.3 The Effect of Temperature and Viscosity on the Model 96
4.4 The Effect of Diameter Size on the Model 98
4.5 The Effect of Salt Concentration on the Model 100
4.6 The Effect of Hamaker Constants on the Model 103
4.7 The Effect of Fractal Dimension and Primary Particle Sizes on the Model 105
4.8 The Effect of Surface Potential on the Model 108
4.9 The Effect of Shear Rate on the Model 110
4.10 The Effect of Simultaneous Perikinetic and Orthokinetic Collision Mechanisms 111
4.11 Summary 122

CHAPTER 5: COMPARISON OF MATHEMATICAL MODEL WITH EXPERIMENTS 123

5.1 Introduction 123
5.2 Materials 123
5.3 Particle Size Distributions 125
5.4 Measurement of Surface Potentials 125
5.5 Measurement of Aggregation Phenomenon 126
5.6 Experimental Runs 127
5.7 Comparison 128
  5.7.1 Experiment A 128
  5.7.2 Experiment B 133
  5.7.3 Experiment C 138
  5.7.4 Experiment D 143
LIST OF TABLES

Table 3.1. Table of Aggregation Events for the Method of Litster et al. 80
Table 3.2. Table of Aggregation Events for the Method of Litster et al. (Updated) 85
Table 4.1 Discretizing Parameter versus Total Number of Bins 94
Table 4.2. Experimental Parameters for Perikinetic and Orthokinetic Experiments 113
Table 5.1. Properties of Particle Standards 124
Table 5.2 Properties of Particle Stock Solutions 124
Table 5.3 Summary of the Initial Particle Size Distribution for Standards 125
Table 5.4. Experimental Parameters for Experiment A 128
Table 5.5. Degree of Aggregation for Experiment A 128
Table 5.6. Experimental Parameters for Experiment B 133
Table 5.7. Degree of Aggregation for Experiment B 133
Table 5.8. Experimental Parameters for Experiment C 138
Table 5.9. Degree of Aggregation for Experiment C 138
Table 5.10. Experimental Parameters for Experiment D 143
Table 5.11. Degree of Aggregation for Experiment D 143
Table 5.12. Experimental Parameters for Experiment E 148
Table 5.13. Degree of Aggregation for Experiment E 148
Table 5.14. Experimental Parameters for Experiment F 150
Table 5.15. Degree of Aggregation for Experiment F 150
LIST OF FIGURES

Figure 2.1. The Gouy-Chapman Model 9
Figure 2.2. Double Layer Structure 10
Figure 2.3. Potential Profile for Gouy-Chapman Model 10
Figure 2.4. Perikinetic Aggregation 16
Figure 2.5. Boundary Conditions for Smoluchowski’s Fast Coagulation Equation 17
Figure 2.6. Movement of Particles in Shear Flow 19
Figure 2.7. Movement of Particles in Extensional Flow 20
Figure 2.8. Comparison of Collision Rate Constants for Different Transport Mechanisms 23
Figure 2.9. Difference Between Rectilinear and Curvilinear Trajectories 25
Figure 2.10. Collision Efficiency as a Function of Shear Rate and Particle Size 26
Figure 2.11. Limiting Stability Ratio \( W_{\text{lim}} \) as a Function of the Hamaker Constant (---) 28
Figure 2.12. Potential Energy Curve for Colloidal Interaction. 30
Figure 2.13. Population Balance Modeling 39
Figure 2.14. Arrangement for Different Number of Primary Particles 40
Figure 2.15. Construction Process of the Prefractal Koch Curves. 41
Figure 2.16. Schematic Illustration of Self-Similar Aggregate Structure 43
Figure 2.17. 3-D Representation of Several Aggregates with \( D_f = 1.5 \to 2.5 \). 44
Figure 2.18. Comparison between the Coalescence and Fractal Aggregate Model 45
Figure 3.1. Contact of Two Dissimilar Spheres 50
Figure 3.2. Potential Energy of Interaction for Different Particle Sizes 51
Figure 3.3. Potential Energy of Attraction for Different Particle Sizes 52
Figure 3.4. Potential Energy of Attraction for Different Particle Sizes 52
Figure 3.5. Potential Energy of Repulsion for Different Particle Sizes 54
Figure 3.6. Potential Energy of Repulsion for Different Particle Sizes 54
Figure 3.7. Graphical Depiction of the Method of Papadopoulos and Cheh 56
Figure 3.8. Flowsheet for Numerical Integration of Non-Linear PBE 61
Figure 3.9. PBE Interaction Energy Comparison 63
Figure 3.10. PBE Interaction Energy Comparison 64
Figure 3.11. PBE Interaction Energy Comparison 65
Figure 3.12. PBE Interaction Energy Comparison 66
Figure 3.13. PBE Interaction Energy Comparison 67
Figure 3.14. Perikinetic Rate Constants 68
Figure 3.15. Orthokinetic Rate Constants 69
Figure 3.16. Differential Settling Rate Constants 70
Figure 3.17. Stability Ratios for HHF 72
Figure 3.18. Stability Ratios for RKF and Papadopoulos 72
Figure 3.19. Stability Ratios for Orthokinetic Collision Mechanism 73
Figure 3.20. Stability Ratios for Orthokinetic Collision Mechanism 74
Figure 3.21. Log of Aggregation Coefficients for Perikinetic Collision Mechanism 75
Figure 3.22. Log of Aggregation Coefficients for Orthokinetic Collision Mechanism 76
Figure 3.23. Log of Aggregation Coefficients for Differential Settling Mechanism 76
Figure 3.24. Discrete Bins to Cover a Large Range of Particle Sizes 78
Figure 3.25. Moments versus $I_{\text{agg}}$ 88
Figure 3.26. Error in the jth Moment for Size-Dependent Case 90
Figure 3.27. Error in the jth Moment for Size-Independent Case 91
Figure 3.28. Flow Diagram of Mathematical Model 92
Figure 4.1. Comparison of Discretizing Parameters for Perikinetic Collision Mechanism 95
Figure 4.2. Comparison of Discretizing Parameters for Orthokinetic Mechanism 96
Figure 4.3. Temperature Comparison 97
Figure 4.4. Viscosity Comparison 98
Figure 4.5. Diameter Size Comparison for Perikinetic Aggregation 99
Figure 4.6. Diameter Size Comparison for Orthokinetic Aggregation 99
Figure 4.7. Effect of Ionic Strength on Interaction Energy for Clay Mineral Kaolinite 101
Figure 4.8. Effect of Ionic Strength on Clay Mineral Kaolinite. 102
Figure 4.9. Ionic Concentration Comparison for the Model 103
Figure 4.10. Potential Energy of Interaction for Various Values of Hamaker Constant 104
Figure 4.11. Hamaker Constant Comparison 105
Figure 4.12. Comparison of Primary Particle Size for Perikinetic Collision Mechanism 106
Figure 4.13. Comparison of Primary Particle Size for Orthokinetic Collision 107
Figure 4.14. Fractal Dimension Comparison for Perikinetic Collision 107
Figure 4.15. Fractal Dimension Comparison for Orthokinetic Collision Mechanism 108
Figure 4.16. Constant Surface Potential Between Two Plates 109
Figure 4.17. Scaling Surface Potential Between Two Plates 109
Figure 4.18. Surface Potential Versus Diameter 110
Figure 4.19. Comparison of Shear Rates 111
Figure 4.20. Peclet Number Versus Particle Diameter 112
Figure 4.21. Log of Aggregation Coefficient, $G = 1$, Peclet < 1 114
Figure 4.22. Log of Stability Ratios, $G = 1$, Peclet < 1 114
Figure 4.23. Log of Stability Ratios, $G = 70$, Peclet < 1 115
Figure 4.24. Log of Stability Ratios, $G = 70$, Peclet < 1 115
Figure 4.25. Perikinetic and Orthokinetic Aggregation 116
Figure 4.26. Log of Aggregation Coefficient for $G = 10$ and the Peclet number <290 117
Figure 4.27. Log of Stability Ratios for $G = 10$ and the Peclet number <290 117
Figure 4.28. Log of Aggregation Coefficient for $G=20$ 118
Figure 4.29. Log of Stability Ratios for $G=20$ 118
Figure 4.30. Perikinetic and Orthokinetic Aggregation 119
Figure 4.31. Log of Perikinetic and Orthokinetic Collision Mechanism where $G = 20$ 120
Figure 4.32. Log of Stability Ratios for $G = 20$ 120
Figure 4.33. Log of Aggregation Coefficients for $G = 20$ 121
Figure 4.34. Addition of Perikinetic and Orthokinetic Aggregation 121
Figure 5.1. Zeta Potential for Polystyrene 126
Figure 5.2. Log of Perikinetik Collision Mechanism for Experiment A 129
Figure 5.3. Log of Stability Ratios for Experiment A 129
Figure 5.4. Log of Aggregation Coefficient for Experiment A 130
Figure 5.5. Particle Concentration versus Time for Experiment A 130
Figure 5.6. Particle Concentration versus Particle Diameter for Experiment A 131
Figure 5.7. Actual versus Mathematical Model Experiments (Experiment A) 132
Figure 5.8. Log of Perikinetik Collision Mechanism for Experiment B 134
Figure 5.9. Log of Stability Ratios for Experiment B 134
Figure 5.10. Log of Aggregation Coefficients for Experiment B 135
Figure 5.11. Particle Concentration versus Time for Experiment B 135
Figure 5.12. Particle Concentration versus Particle Diameter for Experiment B 136
Figure 5.13. Actual versus Mathematical Model Experiments (Experiment B) 137
Figure 5.14. Log of Orthokinetic Collision Mechanism for Experiment C 139
Figure 5.15. Log of Aggregation Coefficient for Experiment C 139
Figure 5.16. Particle Concentration versus Time for Experiment C 140
Figure 5.17. Particle Concentration versus Particle Diameter for Experiment C 140
Figure 5.18. Log of Stability Ratios for Experiment C 141
Figure 5.19. Actual versus Mathematical Model Experiments (Experiment C) 142
Figure 5.20. Stability Ratios for Experiment D 144
Figure 5.21. Log of Orthokinetic Collision Mechanism for Experiment D 144
Figure 5.22. Log of Aggregation Coefficients for Experiment D 145
Figure 5.23. Particle Concentration versus Time for Experiment D 145
Figure 5.24. Particle Concentration versus Particle Diameter for Experiment D 146
Figure 5.25. Actual versus Mathematical Model Experiments (Experiment D) 147
Figure 5.26. Actual versus Mathematical Model Experiments (Experiment E) 149
Figure 5.27. Actual versus Mathematical Model Experiments (Experiment F) 151
LIST OF SYMBOLS

Alphanumeric Symbols

A          effective Hamaker constant
a          primary particle radius
a,b        constants in Cauchy equation
a_i        activity coefficient of ion i
a_i        radius of particle with size i
B          birth function
C          concentration of particles
C          Constant
C_1,C_2    volume correction factors in discretization method
D          death function
D_f        mass fractal dimension
D_i        diffusion coefficient of particle with size i
e          electron charge
F          Faraday Constant
F          growth rate of particles along the size axis
g          acceleration due to gravity
$\bar{G}$ average shear rate

$G$ shear rate

$I_{agg}$ degree of aggregation

$I_i$ modified Bessel function of the first kind order one

$J_i$ flux of particle of size $i$

$k$ Boltzmann constant

$k_{1(\lambda)}$ absorption coefficient for particulate matter as a function of wavelength

$k_f$ fast aggregation rate constant

$K_i$ fraction of successful collisions for each type $i$ in discretization procedure

$k_{ij}$ rate constant of aggregation between particle of size $i$ and $j$

$l$ kinematic viscosity

$l_c$ center to center particle separation

$L$ length size coordinate

$l_p$ path length

$M$ mass of aggregate

$m$ complex refractive index

$m_j$ $j$th moment of the particle size distribution

$\bar{m}_j$ dimensionless $j$th moment of the particle size distribution

$n$ number concentration of negative ions

$n(L,t)$ population density function in length coordinates

$n(v,t)$ population density function in volume coordinates

$n_+$ number concentration of positive ions

$x$
\( n_0 \) number concentration of ions

\( N_0 \) total initial number of particles

\( n_0(\lambda) \) refractive index of medium as a function of wavelength

\( n_1(\lambda) \) refractive index of the particulate matter as a function of wavelength

\( N_D(D,t) \) number density function on a diameter basis

\( N_i \) number concentration of particles in size range \( i \)

\( n_k \) kolmogoroff microscale

\( N_p \) total number of particles in turbidity equation

\( N_v(v,t) \) number density function on a volume basis

\( P \) combined regional and property space

\( q \) adjustable discretization parameter

\( R \) Ideal Gas Constant

\( r \) particle radius

\( R' \) region of property space for all \( m \)

\( r_g \) geometric ratio

\( R_i \) radius of particle with size \( i \)

\( R_{ij} \) collision radius between particles of size \( i \) and \( j \)

\( S \) arc length in Papadopolous integration technique

\( S(P) \) function to relate important interval limits in discretization procedure

\( S_A \) Surface Area

\( T \) Temperature

\( V' \) region of dimensional space
\( V_A \) van der Waals attractive interaction energy

\( v_e^i \) propagation through property coordinate \( i \)

\( V_f \) interaction energy per unit area of between two parallel plates

\( v_i \) volume of particle in in size range \( i \)

\( v_o \) mean initial particle volume

\( V_{\text{part}} \) volume of particles

\( V_R \) electrostatic repulsive interaction energy

\( V_T \) total interaction energy

\( \bar{v} \) average propagation velocity in all property space

\( \bar{v} \) dimensionless volume

\( W_{ij} \) stability ratio between particles of size \( i \) and \( j \)

\( x,y,z \) spatial coordinates

\( Xd \) separation between plates

\( X_{\text{ref}} \) distance between plates corresponding to a particular solution

\( Z \) total number of discretization bins

\( z_i \) valence of ion \( i \)

**Greek Symbols**

\( \alpha \) collision efficiency

\( \alpha_m \) Mie size parameter

\( \alpha_o \) size independent aggregation constant
\( a_{ij} \) aggregation coefficient between particles of size i and j

alternate volume coordinate

dielectric permittivity

power input per unit volume

Debye-Huckel parameter

alternate length coordinate or wavelength

Electrostatic potential

initial aggregate density, (1-porosity)

aggregate density of particle with radius \( R_i \)

Surface potential

reduced surface potential

density

density of fluid

density of particle

dimensionless aggregation time

residence time

turbidity for wavelength \( l \)

population density function

angles used in Papadopolous integration technique

moment generating function viscosity

property space
A MATHEMATICAL MODEL OF COLLOIDAL AGGREGATION

Colleen O’Brien

ABSTRACT

The characterization of fine particles is an area of immense significance to many industrial endeavors. It has been estimated that 70% of all industrial processes deal with fine particles at some point in the process. A natural phenomenon occurring in these processes is colloidal aggregation. This study examines aggregation in colloidal systems in order to characterize, examine, and control this occurrence in industrial processes. The study of particle aggregation has been broken into many different areas, such as collision mechanisms, interaction energy etc, but a complete model that integrates these different aspects has never been fully realized. A new model is required to accurately predict the aggregation behavior of colloidal particles.

In this work, a new model is developed that integrates Smoluchowski kinetics, total interaction energy between particles, and stability ratios for perikinetic and orthokinetic collision mechanisms. The total particle interaction energy necessary for the calculation of stability ratios is represented by the summation of electrostatic and van der Waals
interactions. The electrostatic interactions are modeled using DLVO theory, the linear Poisson-Boltzmann equation, and a numerical solution for the non-linear Poisson-Boltzmann Equation, while the van der Waals interactions are represented by Hamaker theory. The mathematical model is solved using an adjustable discretion technique, which is tested against a specific analytic solution, and yields an assessment of the error intrinsic in the discretization method. The basis of the mathematical model is a population balance framework. The model developed in this study is general in many respects, but could be readily applied to many different aggregation systems with minor modification.

A comparison of the mathematical model with previous experiments conducted by Scott Fisher (1998) is carried out for the perikinetic and orthokinetic transport-limited aggregation regimes. The fractal nature of solid-sphere aggregates is considered when comparing the mathematical model predictions with experimental measurements. The previous experiments that are used for comparison utilized polystyrene particles ranging from 100nm to 500nm in initial diameter, several initial particle concentrations, and various stirring rates. Zeta potential measurements are presented in order to set the range of transport-limited aggregation. An assessment of the results of the mathematical model with the experimental results show good agreement for transport-limited aggregation within the perikinetic and orthokinetic transport-limited aggregation, with average particle sizes ranging from 100nm to well over 2 μm.
CHAPTER 1: INTRODUCTION

Aggregation has become increasingly significant during the last twenty-five years. Industry has become progressively more interested in controlling the microscopic properties of particles, such as composition, shape, surface roughness, surface characteristics, and porosity. It has been estimated that 70% of all industrial processes involve dealing with fine particles at some point in the process (Bushell 1998). Characterization of these particles help us to understand and predict or control their behavior in many processes. In industry, the properties of particles determine whether or not a dust is a respiration hazard, whether granular materials will mix or segregate when agitated, and whether material in a hopper will flow in a controllable fashion, behave like a liquid, or not flow at all.

Many of the traditional particle characterization techniques make assumptions about the shape or physical structure of the particles being measured. The extraction of linear-size parameters from laser scattering measurements generally assume that the particles are spherical. This assumption is normally made because it probably is not important to the technique being used, but often it is because it is a difficult problem.

One class of particles that has great importance is aggregates. Almost every particulate system involves to a greater or lesser extent some particles that are aggregates of smaller particles in the system. This may be unimportant for systems such as the handling of bulk ores, but in processes such as drinking water filtration, it is the dominant structure. These aggregates are often wispy, tenuous entities that are absolutely unlike spheres, plates, or other familiar geometric forms. The equations used in this model are for spherical particles, but the spherical particles are translated into their associate fractal dimension at the end of the model.
The beginning of the current understanding of colloidal aggregation dates back to the work of Smoluchowski (1917). He identified aggregation as a second-order process dependent on the concentration of aggregating species. The early work in this area consisted of measuring and predicting rates of aggregation based upon single equations. Up until the mid-seventies, the study of aggregation considered only the formation of distinct aggregates from a monodispersed (uniform in shape and size) initial particle system, or the calculation of rate constants of aggregation from doublet formation.

The nature and magnitude of various forces acting on the particles determine the stability of the suspension. Generally, in case of a solid dispersion in an aqueous medium, the forces acting on a particle include van der Waals forces, electrostatic forces and hydrodynamic forces. Of these, the van der Waals forces are attractive in nature and favor aggregation. Electrostatic forces exist due to the presence of an electric double-layer around the particles and cause repulsion between the particles. This has the effect of opposing aggregation. Both of these forces are similar in magnitude, and act over comparable distances from the particle surface. If the electric double-layer repulsion dominates, the suspension remains stable, and does not agglomerate. However, suppressing the electric double-layer can destabilize a suspension making the van der Waals attractive forces dominant, and creating aggregation. This kind of aggregation is known as “coagulation”.

When particles collide with each other, not all collisions result in the formation of agglomerates. Instead, only a fraction of the total collisions lead to the formation of agglomerates. This fraction is known as the collision efficiency, and it determines the overall rate of aggregation. When a suspension is sheared, the particulate size increases as aggregation takes place. However, stresses develop at the same time due to fluid shearing and tend to break up the agglomerates into a smaller size. Hence, during the flow of a suspension, particle enlargement and breakage take place simultaneously. Consequently, agglomerates do not continue to grow indefinitely in size during prolonged shearing; instead they attain an equilibrium size.
This paper is a summation of the work of Luis H. Garcia-Rubio’s colloidal particle students over the last decade. The major contributions are by Esteban Marquez-Riquelme (1994) in the area of the non-linear Poisson-Boltzmann equation to obtain the repulsive interaction energies between spherical particles, and Scott Fisher (1998) who researched and implemented the population balance equations with the Litster et al. (1995) method of discretization. The three major sections of this paper are (1) the mathematical model description, (2) The investigation of the mathematical model, and (3) a validation of the model against a set of aggregation experiments that were performed by Scott Fisher (1998). In accomplishing these goals, the work is outlined in the following matter: Chapter 2 deals with the background information that is necessary to understand the model. Chapter 3 outlines the general mathematical model for aggregation phenomenon. Chapter 4 deals with an investigation of the model parameters. Chapter 5 provides a comparison between the mathematical model predictions and the measured aggregation phenomena. Chapter 6 deals with a general summary and conclusions, as well as future development of the model.
CHAPTER 2: AGGREGATION THEORY

2.1 Introduction
This chapter describes the necessary background topics required to understand the mathematical model for aggregation. The first section describes the basic properties of colloidal particles. The next few sections describe aggregation kinetics, collision mechanisms, particle stability, and aggregate structure. The attractive and repulsive forces, such as electrostatic repulsive and van der Waals attractive forces, will then be discussed. Next, a mathematical introduction to the population balance model is included. The theory presented in this chapter introduces the basic concepts necessary to understand the mathematical model.

2.2 Colloidal Particles
Colloids form heterogeneous mixtures that are large enough to scatter light. Colloids usually consist of two phases, or one continuous phase in which the other phase is dispersed. These particles are larger than the size of molecules, but small enough for the dispersed phase to stay suspended for a long period of time.

Colloidal systems contain at least one or more substances that have at least one dimension in the range between $10^{-9}$ m (10 Å) and $10^{-6}$ m (1 μm) in size (Hiemenz, 1986). On the smaller end of this scale, there are no distinct boundaries between the phases, and the system is considered a solution. On the larger end of this scale, particles will begin to fall to the bottom due to gravitational force, and the phases are separated. Aggregation involves the association of particles to form clusters, and depends on two distinct influences: (1) particles must move in a way that collisions occur, and (2) particles that repel each other are said to be stable, since they do not form aggregates. Colloids interact with each other at
an extremely short range, (usually much less than the particle size), so that particles have to approach very close to each other before any significant interaction is felt. The interaction may be attractive (van der Waals) or repulsive (electrostatic repulsion, steric).

There are many important properties of colloidal systems that are determined directly or indirectly by the interaction forces between particles. These colloidal forces consist of the electrical double layer, van der Waals, Born, hydration, and steric forces. Colloidal particles are dominated by surface properties. If the surface area to volume, or surface area to mass of a spherical particle is looked at, the dependence on the particle radius is \( S_A/V \mu \) \( 1/r \). This relationship shows that as particles decrease in size, the surface properties of the particle become increasingly important (Fisher, 1998). The measurement of particle size is also a defining property. Optical microscopy relies on visible light, which renders colloidal particles largely invisible to optical techniques. (Visible light limits measurements to about 0.5 \( \mu \)m). Sedimentation cannot be used to characterize particles because the particles need to be about 1.5 \( \mu \)m in size (Fisher, 1998).

2.3 Surface Charge
Colloidal suspensions usually consist of charged particles dispersed throughout a continuous solvent phase. When two phases are in contact, a separation of charge will occur which causes a difference in electrical potential. If this phase separation is restricted to a solid interface with an aqueous electrolyte system, there are several possible mechanisms for the separation of charge:

1) a difference in affinity of ions for the two phases

2) ionization of surface groups

3) physical restriction of certain ions to one phase.

The first case of separation of charge is usually found in metal halides, calcium carbonate, and metal oxides. The best-known example is silver iodide (Elimelech et al., 1995). When silver iodide is in contact with pure water, silver ions have a tendency to escape from the
crystal lattice, leaving a crystal with an excess negative charge. If the concentration of silver ions is increased, a point is reached where the higher escaping tendency of the silver ions is balanced by their higher concentration in solution, and the solid does not have a net charge (Elimelech et al., 1995). For these cases, the surface potential, $\Box_0$, can be modeled by the Nerst equation:

$$\Box_0 = \text{constant} + \frac{RT}{z_i F} \ln a_i$$  \hspace{1cm} (2.3.1)$$

where R is the gas constant, T is the absolute temperature, F is the Faraday constant, $z_i$ is the valence, and $a_i$ is the activity of the escaping ions (Elimelech et al., 1995).

An example of pH-dependent surface charge is the case of metal oxides. When metal oxides are in contact with water, the oxide surfaces become hydroxylated, giving the possibility of surface ionization to yield either positive or negative groups. The ionization of such groups can be written as:

$$\text{S—OH}_2^+ \Box \text{ S—OH} \Box \text{ S—O}^-$$

Where S denotes a solid surface (Elimelech et al., 1995). This process involves the loss of two protons, which are defined by appropriate equilibrium constants. The degree of protonation depends on the values of these equilibrium constants and the solution properties.

2.4 Gouy-Chapman Model

If the colloidal particles in solution are charged, and the solution is electrically neutral, the balancing charge is accounted for by an excess number of oppositely charged ions or counterions in solution adjacent to the charged surface and a deficit of similarly charged ions. In this electrical double layer, the counterions are distributed according to a balance between their thermal motion and the forces of electrical attraction. The Gouy-Chapman
model characterizes this arrangement of charged species around the colloidal particle. The electronic double layer is composed of two layers, the inner layer (Stern layer), and the outer layer (diffuse layer). The Stern layer consists mainly of oppositely charged ions adsorbed to the colloid surface. The diffuse layer consists of a mixture of ions extending some distance away from the colloid. The Shear surface is the surface between the fixed and diffuse layer and defining the mobile portion of the colloid. A diagram of the electric double layer is shown in Figures 2.1 (Anderson et al., 1975) and 2.2 (Marquez, 1994). A diagram of the potential profile for Gouy-Chapman Model in shown in Figure 2.3 (Anderson et al., 1975).

![Figure 2.1. The Gouy-Chapman Model](image)
Figure 2.2. Double Layer Structure

Figure 2.3. Potential Profile for Gouy-Chapman Model
The Gouy and Chapman model is based on a number of simplifying assumptions:

1) an infinite, flat impenetrable interface

2) ions in solution are point charges, able to approach right up to the interface.

3) the surface charge and potential are uniformly ‘ smeared out’ over the surface.

4) the solvent is a uniform medium with properties (especially permittivity) that are independent of distance from the surface.

The relationship between charge density, \( \sigma \) (cm\(^{-3}\)), and potential, \( \psi \), at any point is the Poisson equation:

\[ \nabla^2 \psi = \frac{\rho}{\varepsilon} \]  \hspace{1cm} (2.4.1)

where \( \varepsilon \) is the permittivity of the medium. The Boltzmann Distribution gives the distribution of positive and negative ions away from the particle surface:

\[ n_+ = n_0 \exp \left( \frac{ze\psi}{kT} \right) \] \hspace{1cm} (2.4.2)

\[ n_- = n_0 \exp \left( \frac{-ze\psi}{kT} \right) \]

where \( n_+ \) and \( n_- \) are the number of cations and anions per unit volume with charge +e and –e respectively. \( N_0 \) is the number of anions or cations far from the surface where the average electrostatic potential \( \psi \) is zero. \( T \) is the absolute temperature and \( k \) the Boltzmann constant, and \( z \) is the valence of electrons (Elimelech et al., 1995).
Since a flat interface is being considered, the Poisson-Boltzmann expression will be used:

$$\frac{d^2 \Box}{dx^2} = \frac{2ze_n}{\Box} \sinh \frac{ze}{kT}$$

(2.4.3)

The dimensionless parameters are: $y = \frac{ze}{kT}$ and $X = \frac{x}{\Box}$, where $\Box$ is given, for z-z electrolytes, by:

$$\Box^2 = \frac{2e^2n_zz^2}{\Box kT}$$

(2.4.4)

The Debye-Huckel parameter, $\Box$, has the dimensions of reciprocal length and plays a very important part in the electrical interaction between colloidal particles. Substituting $y$ and $X$:

$$\frac{d^2 y}{dX^2} = \sinh y$$

(2.4.5)

The Gouy-Chapman theory has several short-comings. For example, measured capacitances at certain interfaces can be much lower than predicted by theory. Also, counterions concentrations close to charged interfaces can become unreasonably high, even for moderate values of surface potential (Marquez, 1994).

2.4.1 Diffuse Layer Model

The surface charge density is given by:

$$\Box = \frac{\Box_{tot} e}{1 + a_{it}^S / K}$$

(2.4.6)

where $e$ is the protonic charge, $\Box_{tot}$ the total density of chargeable sites, $a_{it}^S$ demotes the surface activity of the protons, and $K$ is the dissociation constant (Behrens et al., 1999).
The charge of a latex surface can be related to the solution properties with the so-called diffuse layer model (DLM). This model assumes that all the surface charge is located at the solution interface, which is characterized by the electrostatic surface potential $\psi_0$. The proton activity at the surface is evaluated as:

$$a_H^s = a_H \exp(\psi_0)$$  \hspace{1cm} (2.4.7)

where pH$=-\log a_H$, and $k_B$ the thermal energy (Behrens et al., 1999). These equations define a relation between the surface charge and surface potential. Equilibrium requires the simultaneous fulfillment of a second charge-potential relation that follows from the distribution of mobile ions in the diffuse layer. In a description based upon the Poisson-Boltzmann equation for 1-1 electrolytes, the surface charge density $\mathcal{Q}$ of an isolated particle with radius, $R$, can be expressed in terms of the surface potential $\psi_0$ as:

$$\mathcal{Q} = \frac{2\varepsilon_0}{\varepsilon_0} \sinh(\psi_0 / 2) + \frac{2}{\varepsilon_0 R} \tanh(\psi_0 / 4)$$  \hspace{1cm} (2.4.8)

where $\varepsilon_0$ is the total permittivity of the solution and $1/\varepsilon_0 = \sqrt{\varepsilon_0}/(2N_A\varepsilon_0^2)$ the Debye length, further involving the ionic strength $I$ ($N_A$ is Avogadro’s number). Without the second term on the right side, this is just the classical Gouy-Chapman result. The additional term was proposed by Loeb, Overbeek, and Wiersema, and gives a first order correction for the surface curvature, accurate to within 5% of the true charge density for any surface potential whenever the Debye length is smaller than the particle diameter (Loeb, Overbeek, Wiersema, 1961). The last three equations determine the equilibrium value of the surface charge $\mathcal{Q}$ and potential $\psi_0$ at a given pH (Behrens et al., 2000).

2.4.2 Electrophoretic Mobility and Zeta Potential
For a flat surface in a monovalent electrolyte, the electrostatic potential at a distance $x$ from the surface is related to the surface potential $\psi_0$ via:
\[ \square(x) = \frac{4}{e^{k} - e^{-k}} \arctan(h[\exp(\frac{k}{e})] \tanh(\frac{k}{e} \beta / 4) \] (2.4.9)

as follows from the integration of the Poisson-Boltzmann equation. The zeta potential was computed as the electrostatic potential \( \zeta = \zeta(x) \) at some distance \( x \), from the surface, corresponding to the thickness of an immobile fluid layer, adjacent to the particle surface (Behrens et al., 2000). The outer end of this immobile layer, where the motion of fluid relative to the particle sets in, is commonly referred to as the surface of shear.

2.5 Aggregation
Three of the most basic properties of a particulate system are the particle composition, particle size distribution, and particle shape. As particles undergo aggregation, the particle size distribution and shape of the particle can change dramatically—depending on the fractal nature of the aggregate structure. The foundations of the rate of aggregation start from the classic work of Smoluchowski (1917). It is convenient to think in terms of a dispersion of initially identical particles, which, after a period of aggregation, contains aggregates of various sizes and different concentrations. A fundamental assumption is that aggregation is a second-order rate process, in which the collision is proportional to the product of concentrations of two colliding species (Elimelech et al., 1995). Three-body collisions are usually ignored in treatments of aggregation—they usually become important at very high particle concentrations. The number of collisions occurring between i and j particles in unit time and unit volume, \( J_{ij} \), is given by:

\[ J_{ij} = k_{ij} n_{i} n_{j} \] (2.5.1)

Where \( k_{ij} \) is a second rate order constant, which depends on a number of factors, such as particle size and transport mechanism.

In considering the rate of aggregation, it must be recognized that not all collisions may be successful in producing aggregates. The fraction of successful collisions is called the collision efficiency and is given the symbol \( \theta \). If there is strong repulsion between particles, there will not be any collisions that give aggregates and \( \theta = 0 \). When there is no
significant net repulsion or attraction between particles, then the collision efficiency can approach unity (Elimelech et al., 1995).

It is normal to assume in aggregation modeling that the collision rate is independent of colloid interactions and depends only on particle transport. This assumption can be justified on the basis of the short-range nature of interparticle forces, which operate over a range which is usually much less than the particle size, so that the particles are nearly in contact before these forces come into play. For the present, it shall be assumed that every collision is effective in forming an aggregate (collision efficiency, $\bar{k}=1$), so that the aggregation rate constant is the same as the collision rate constant. The rate of change of concentration of $k$-fold aggregates, where $k = i + j$:

$$\frac{dn_k}{dt} = \frac{1}{2} \prod_{i+j<k} k_{ij} n_in_j \prod_{i=k} n_i \prod_{i=k} k_{ik} n_i$$  

(2.5.2)

The first term on the right-hand side represents the rate of formation of $k$ aggregates by collision of any pair of aggregates, $i$ and $j$, such that $i + j = k$. Carrying out the summation by this method would mean counting each collision twice and hence the factor $\frac{1}{2}$ is included. The second term accounts for the loss of $k$ aggregates by collision, and aggregation, with any other aggregates. The terms $k_{ij}$ and $k_{ik}$ are the appropriate rate constants (Elimelech et al., 1995). The above equation is for irreversible aggregation.

2.6 Models for Collision Rates

The determination of rate constants for aggregation events is dependent on two factors: (1) the mechanism by which particle collisions occur, and (2) the presence of interparticle interactions.

In considering the nature of particle transport, and correspondingly particle collision, there are three major mechanisms (1) Brownian motion (Perikinetic aggregation), (2) fluid motion (Orthokinetic aggregation), and (3) differential sedimentation (Elimelech et al., 1995). These mechanisms will be discussed in the next few sections. In all cases it is
assumed that particles are spherical and that the collision efficiency is unity. Hydrodynamic interaction will be neglected in the next few sections.

2.6.1 Perikinetic Collision Mechanism
Small particles in suspension can be seen to undergo continuous random movements called Brownian motion. This phenomenon occurs primarily in particles 100 nm to 1000 nm (Peltomaki, 2002). Brownian motion is temperature dependent, and becomes increasingly important when particles are one micron or smaller. It is also important under conditions of high particle concentration (greater than 10 g/L), and low or no shear (Ernest, 1995). The motion of perikinetic aggregation is shown in Figure 2.4 (Ernest, 1995).

![Perikinetic Aggregation](image)

Figure 2.4. Perikinetic Aggregation

Smoluchowski derived an expression for collision frequency in this case by considering the diffusive flux of the particles towards a stationary particle (Agarwal, 2002). Using Fick’s law for the number of particles \( J' \) going through a unit area toward a reference particle per unit time:

\[
J' = D \frac{dN}{dr}
\]

(2.6.1)

where \( D \) is the diffusion coefficient of particles, \( N \) is the number concentration, and \( r \) is the radial distance from the center of the reference particle. Smoluchowski defined a spherical surface around a reference particle (Figure 2.5) so that any other particle whose center
passes through that boundary will be considered to collide effectively and produce coagulation (Marquez, 1994).

\[
J' = \Theta(4\pi r^2)D \frac{dN}{dr}
\]  

(2.6.2)

Figure 2.5. Boundary Conditions for Smoluchowski’s Fast Coagulation Equation

The number of particles going through a sphere of radius \( r \) in unit time is:
The diffusion coefficient of a spherical particle is given by the Stokes-Einstein equation:

\[ D_i = \frac{kT}{6\eta_i} \]  

(2.6.3)

where \( k \) is the Boltzmann’s constant, \( T \) is the absolute temperature, \( a_i \) the particle radius, and \( \eta \) the viscosity of the suspending fluid (Elimelech et al., 1995). Smoluchowski (1917) calculated the rate of diffusion of spherical particles of type \( i \) to a fixed sphere \( j \):

\[ J_i = 4\eta R_{ij} D_i n_i \]  

(2.6.4)

Where \( D_i \) is the diffusion coefficient of particles of type \( i \) and \( n_i \) is their concentration in the bulk expression. This collision radius can be considered the center-to-center distance at which a contact takes place. This is simply the sum of the particle radii: \( R_{ij} = a_i + a_j \) (Elimelech et al., 1995).

In reality, the central sphere \( j \) is not fixed, but is itself subject to Brownian diffusion. If the concentration of \( j \) particles is \( n_j \), then the number of \( i-j \) collisions occurring in the unit volume per unit time is:

\[ J_i = 4\eta R_{ij} D_i n_i n_j \]  

(2.6.5)

The rate constant for aggregation is now:

\[ k_{ij} = \frac{2kT (a_i + a_j)^2}{3\eta a_i a_j} \]  

(2.6.6)

This equation gives the rate constant for perikinetin collisions. For particles of approximately equal size, the collision rate constant becomes almost independent of particle size.
2.6.2 Orthokinetic Collision Mechanism

Collisions brought about by Brownian motion do not usually lead to the rapid formation of large aggregates. Particle transport brought about by fluid motion can give an enormous increase in the rate of interparticle collisions, and aggregation brought about in this way is known as orthokinetic collision. This type of collision becomes relevant between 1 and 10 microns (Peltomaki, 2002). Smoluchowski (1917) also was the first to study the rate of orthokinetic aggregation due to uniform laminar shear forces. A diagram of the movement of particles in shear flow is shown in Figure 2.6 (Agarwal, 2002).

![Diagram of orthokinetic collision mechanism](image)

**Figure 2.6. Movement of Particles in Shear Flow**

A uniform laminar shear field is one in which the fluid velocity varies linearly in only one direction, perpendicular to the direction of flow. Smoluchowski assumed that particles would flow in straight lines and collide with particles moving on different streamlines according to their relative position. The collision frequency depends on the sizes of the particles and on the velocity gradient or shear rate $G$ (Elimelech et al., 1995). By considering a fixed central sphere of radius $a_j$ and flowing particles of radius $a_i$, it can be assumed that those moving particles on streamlines that bring their centers within a distance $(a_i + a_j)$. The collision frequency can then be calculated by considering the flux of
particles through a cylinder of radius $R_{ij}$, the axis which passes through the fixed sphere $j$. The total flux towards the center particle, $J_i$ is just twice that in one half of the cylinder and is given by:

$$J_i = 4Gn_i \int_0^{R_{ij}} \sqrt{\left(R_{ij}^2 - z^2\right)}\,dz = 4Gn_i R_{ij}^3$$  \hspace{1cm} (2.6.7)

The total number of collisions occurring between $i$ and $j$ particles in unit volume and unit time is then simply:

$$J_{ij} = \frac{4}{3} n_i n_j G(a_i + a_j)^3$$  \hspace{1cm} (2.6.8)

The rate constant for orthokinetic collisions between $i$ and $j$ particles is:

$$k_{ij} = \frac{4}{3} G(a_i + a_j)^3$$  \hspace{1cm} (2.6.9)

This equation shows that the rate is proportional to the cube of the collision radius, which has a major effect on aggregate growth rate. As aggregation proceeds and aggregate size increases, the chance of capture becomes greater.

The other major flow field of interest is extensional flow, which is shown in Figure 2.7 (Agarwal, 2002).

![Figure 2.7. Movement of Particles in Extensional Flow](image-url)
In this case the collision frequency is given by:

\[ J = \frac{16}{3} \frac{\nu_{\text{ext}} a^3 N^2}{\nu} \]  \hspace{1cm} (2.6.10)

where \( \nu_{\text{ext}} \) is the strain rate.

2.6.3 Differential Settling Mechanism

Another important collision mechanism arises whenever particles of different sizes and density are settling from a suspension. Particles of different diameters settle at different velocities causing the faster moving particles to collide with slower moving particles leading to aggregation. This type of collision mechanism usually becomes relevant at particles of 10-100 microns in size and larger. By balancing the forces of gravity, buoyancy and drag, the sedimentation velocity of a particle of radius \( a_i \) and density \( \rho_i \) in a medium of density \( \rho \) is given by Stokes’ equation (Agarwal, 2002):

\[ v_i = \frac{2g (\rho_i - \rho) a_i^2}{9 \rho} \]  \hspace{1cm} (2.6.11)

The relative velocity between two particles of diameters \( a_i \) and \( a_j \) would be \( u = v_i - v_j \). The rate of \( N_i \) particles through a cylindrical cross section of \((a_i + a_j)\) is given by:

\[ \frac{dN_i}{dt} = N_i (a_i + a_j)^2 (v_i - v_j) \]  \hspace{1cm} (2.6.12)

Using the last two equations, the resulting collision frequency, for particles of equal density is:

\[ J_{ij} = \frac{2g}{9 \rho} (\frac{\nu_{\text{ext}}}{\nu}) n_i n_j (a_i + a_j)^3 (a_i \cdot a_j) \]  \hspace{1cm} (2.6.13)

where \( g \) is the acceleration due to gravity, \( \rho_i \) is the density of the particles and \( \rho \) is the density of the fluid.
2.7 Comparison of Rates
A summary of the collision mechanisms described in the previous sections are summarized below:

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perikinetic:</td>
<td>( k_p = \frac{2kT (a_i + a_j)^2}{3a_i a_j} )</td>
</tr>
<tr>
<td>Orthokinetic:</td>
<td>( k_{ij} = \frac{4}{3} G(a_i + a_j)^3 )</td>
</tr>
<tr>
<td>Differential Settling:</td>
<td>( k_{ij} = \frac{4}{9} \frac{2kT a_i a_j}{a_i + a_j}(a_i + a_j)^3 )</td>
</tr>
</tbody>
</table>

Usually it is assumed that the three mechanisms of interparticle collisions are independent and when they operate simultaneously the aggregation rates are additive:

\[
J_{total} = J_{Br} + J_{Sedimentation} + J_{Shear} \tag{2.7.1}
\]

The relative magnitudes of each contribution depend on the characteristics of the suspension and flow conditions. If the densities of the particles and the dispersing medium are nearly the same, contribution due to sedimentation can be neglected. Other factors that limit the effect of sedimentation are high viscosity of the dispersing medium and the relatively small size of particles (Bushell, 1998).

For a comparison of rates, it is convinent to take one particle of fixed size and compute the various rate constants as a function of the size of the second particle. To compare the collision frequencies due to shear flow that with due to Brownian motion, their ratio is characterized by the Peclet number (Agarwal, 2002). If \( Pe \gg 1 \), shear flow dominates, but if \( Pe \ll 1 \), Brownian motion will dominate.

\[
Pe = \frac{4a_i a_j}{k_B T} \tag{2.7.2}
\]
As an example, one particle is taken to have a diameter of 1 μm and the other diameter varies between 0.01 and 10 μm. The shear rate is assumed to be 50 s⁻¹ and the density of the particles 2 g/cm³. All other values are appropriate for aqueous dispersions at 25 C.

Figure 2.8. Comparison of Collision Rate Constants for Different Transport Mechanisms.

As shown in Figure 2.8 (Fisher, 1998), it is clear that the perikinetic mechanism gives the highest collision rates for particles less than 0.6 μm in diameter, but for larger particles orthokinetic collisions and differential settling become more important. As the size of the second particle becomes greater than a few microspheres, the collision rate due to sedimentation increases sharply and becomes comparable to the shear-induced rate (Elimelech et al., 1995).
2.8 Collision Efficiencies
In the collisions mechanisms that were discussed so far, it was assumed that all particle collisions are successful in producing aggregates. In reality, this is not the case, and a reduced collision efficiency must be factored in. All that is needed to factor in this rate is to include the collision efficiency, $\eta$, into the rate expressions. There remains the problem of assigning a value to $\eta$, and this will be discussed in the next few subsections.

2.8.1 Perikinetic Collision Efficiencies (Stability Ratio)
The effect of repulsive colloidal interactions on perikinetic aggregation is to give a reduction in rate. In this approach, a stability ratio, $W$, is used and is expressed as $W = 1 / \eta$ (the reciprocal of the collision efficiency). The stability ratio is simply the ratio of the aggregation rate in the absence of colloidal interactions. For cases where only van der Waals attraction and electrical repulsion need to be considered, there is a energy barrier when the particles approach the particles. The stability ratio can be calculated by treating the problem as one of diffusion in a force field:

$$W = 2 \int_0^\infty \frac{\exp(\eta r / kT)}{(u + 2)^2} du$$  \hspace{1cm} (2.8.1)

where $\eta r$ is the total interaction at a particle separation distance $d$, and $u$ is a function of $d$ and particle size. For equal particles, $u = d/a$. It is also been cited as (Marquez, 63):

$$W_{ij} = (R_i + R_j) \int_{R_i, R_j} \exp \left( \frac{V(l)}{k_BT} \right) \frac{dl}{l^2}$$  \hspace{1cm} (2.8.2)

where $V(l)$ is the total interaction energy between particles. To evaluate $W$, the integral in the last equation has to be evaluated numerically, using appropriate expressions for the electrical and van der Waals interactions. Due to the exponential term, most of the contribution to the integral comes from a region close to the maximum.
2.8.2 Orthokinetic Collision Efficiencies
For collisions of non-Brownian particles (> 1 micron), the Fuchs concept of diffusion in a force field is not appropriate and the relative motion of particles induced by fluid shear, or external gravity have to be considered. It has been observed that aggregation of otherwise stable colloids can sometimes be achieved by the application of sufficiently high shear. For a given suspension, the collision efficiency for Brownian aggregation could be very different from that of orthokinetic collisions.

Smoluchowski’s theory makes the assumption that particles travel in straight trajectories along streamlines (streamlines are not disturbed by the presence of particles. However, due to van der Waals, electric double-layer and hydrodynamic interactions, particle trajectories deviate from a straight line as particles approach each other. The difference between rectilinear and curvilinear trajectories is shown in Figure 2.9 (Agarwal, 2002).

![Diagram of rectilinear and curvilinear trajectories](image)

**Figure 2.9. Difference Between Rectilinear and Curvilinear Trajectories**
The net velocity of a particle is given by the sum of velocity fields, which are independent and superposable (Zeichner and Schowalter, 1977):

\[ U = u_{\text{flow}} + u_c \]  

(2.8.3)

The velocity field \( u_{\text{flow}} \) is due to the hydrodynamic flow while \( u_c \) is due to the presence of colloidal forces.

It should be noted that trajectory analysis is valid for calculating the collision efficiency of doublet formation resulting from two primary particles. No theory is available for the calculation of the collision efficiency of aggregated grow from doublets to triplets and larger aggregated because of the complexity of the hydrodynamics involved. The collision efficiency is shown as a function of shear rate in Figure 2.10 (Agarwal, 2002).

Figure 2.10. Collision Efficiency as a Function of Shear Rate and Particle Size
If the electric double layer is completely suppressed by adding an electrolyte, numerical calculations result in an easy expression for collision efficiency (Van de Ven and Mason, 1977):

\[ \mathcal{C} = K \left( \frac{A}{36(2\alpha)} \right)^{0.18} \]  

(2.8.4)

where \( K \) is a constant whose value is close to unity. Potanin (1991) suggested the following expression for aggregation collision efficiency:

\[ \mathcal{C} = \frac{2.1}{(\ln(d / 2\alpha))^{0.29}} \left( \frac{d}{2\alpha} \right)^{0.075} 0.2^{1/2} \]  

(2.8.5)

where \( d \) is the diameter of the aggregate. This expression shows that collision efficiency decreases with increasing \( d \) with respect to primary particle size \( 2\alpha \) (Potanin, 1991). The collision efficiency for orthokinetic collisions cannot be adequately discussed without reference to hydrodynamic interaction.

2.8.2.1 Hydrodynamic Interaction

The Smoluchowski approach to aggregation kinetics takes no account of the effect of the viscosity on the suspending medium. The hydrodynamic or viscous effects can have a great effect on the aggregation rates. As particles approach very close it becomes increasingly difficult for the liquid between them to drain out of the gap, which slows the aggregation process. For orthokinetic and perikinetic aggregation, this resistance will prevent particle contact completely unless a rapidly increasing attractive force such as van der Waals interactions brings the particles together (Spielman, 1978).

The combined effect of van der Waals and hydrodynamic interactions on the limiting stability ratio of spherical particles in water is shown in Figure 2.11 (Elimelech, 1995). For comparison, the finely dotted line also shows the result in the absence of hydrodynamic interaction.

27
Figure 2.11. Limiting Stability Ratio $W_{lim}$, as a Function of the Hamaker Constant (----)

It has been suggested that the colloidal forces between agglomerates are determined by a couple of primary particles whereas hydrodynamic forces are equivalent to forces one would expect between two particles of the size of complete aggregates (Agarwal, 2002). Thus, as the aggregate size increases, hydrodynamic forces increase much more rapidly than colloidal forces resulting in a much lower aggregate collision efficiency than the primary particle collision efficiency (Agarwal, 2002).

From the basic rate of aggregation and the orthokinetic equation, the orthokinetic rate of aggregation becomes (Agarwal, 2002):

$$\frac{dN}{dt} = \frac{16}{3} \sqrt[N]{N^2} j b^3$$  \hspace{1cm} (2.8.6)
If the volume fraction of particles is assumed to remain constant then at any instant, the number concentration of particles can be related to the particle size by \( \frac{4}{3} \pi r^3 N \) (Agarwal, 2002). The last equation can be integrated to obtain:

\[
\ln \frac{N}{N_0} = \frac{4 \pi y \rho}{3 \mu} t 
\]  

(2.8.7)

where \( N_0 \) is the number concentration at time \( t=0 \) and \( N \) is the number concentration at any time \( t \). This equation forms the basis for experimentally determining the collision efficiency. By following the number concentration with respect to time, the last equation gives a straight line during the early stages of aggregation. From the slope of this line, the experimental value of the collision efficiency can be determined (Agarwal, 2002).

2.9 Interparticle Forces

In colloidal systems, there are three basic types of intermolecular forces acting between molecules: (1) Van der Waals forces, (2) Electrostatic forces, and (3) steric hindrance. The combinations of these forces control the type and rate of coagulation in particulate systems. Figure 2.12 (Agarwal, 2002) shows the potential energy curve for colloidal interaction.
2.9.1 Electrostatic Repulsive Forces
The Gouy-Chapman model explains that colloidal particles are surrounded by an electric double layer, where ions are distributed such that the average electrostatic potential is represented by Poisson-Boltzmann equation (PBE). When two particles approach each
other, there is interference between the electrostatic double layers which will result in an increase in energy for the two particles.

2.9.1.1 Sphere-Sphere Interactions
A general formula for the force per unit area between two flat approaching double layers in a symmetrical (z-z) electrolyte was given by Langmuir (1938) and Bell and Peterson (1972):

\[ f_R = n kT \frac{2}{\pi} \cosh \left( \frac{d}{2kT} \right) \frac{d\sigma}{dx} \frac{h}{2} \]  

(2.9.1)

where \( n \) is the bulk number density of ions, \( \sigma = z e \sigma / kT \), and \( \sigma \) denotes the potential at a distance \( x \) from the plate. Integrating the force over distance then gives the potential energy per unit area \( \sigma_R \):

\[ \sigma_R = \frac{h}{2} \int_0^h \frac{d\sigma}{dx} \, dx \]  

(2.9.2)

where \( h \) is the separation of the two surfaces. At equilibrium, \( f_R \) should be equal everywhere. In the sphere-sphere double layer interactions, the most common method for determining interaction energy, based upon the above equations (Derjaguin, 1934) is:

\[ V_R = \frac{2\sigma_1 \sigma_2}{a_1 + a_2} \int_0^h \frac{d\sigma}{dx} \, dx \]  

(2.9.3)

where \( h \) denotes the minimum surface-to-surface separation between the spheres.

No analytical expression exists for the electrostatic interaction on the Poisson-Boltzman level. While computation of the exact double layer energy still requires a considerable numerical effort, the Derjaguin approximation is much more straightforwardly obtained as:
\[ V(h) = \frac{2\mathcal{R}n}{m} \prod_{h} \prod_{y} \cosh[\mathcal{G}[\mathcal{G}[m(x)] m 1] dx dy \quad (2.9.4) \]

where \( n \) is the number density of particles, and \( \mathcal{G}_m(h) \) is the electrostatic potential in the midplane between flat surfaces with the same density of chargeable sites \( \mathcal{G}_{\text{tot}} \). This midplane potential can be calculated by solving the set of equations for \( \mathcal{G} \), \( \mathcal{G}_0 \), and \( \mathcal{G}_m \) that is given by :

\[ \mathcal{G} = \frac{\prod \prod \exp(2\mathcal{G}[\mathcal{G}[m]) \prod^{m} \prod \frac{\text{sn}(v \mid m)}{\text{cn}(v \mid m)dn(v \mid m)} \quad (2.9.5) \]

and \( \mathcal{G}_0 = \mathcal{G}_n + \frac{2}{\mathcal{G}_e} \ln cd(v \mid m) \quad (2.9.6) \]

The functions \( \text{sn}(v \mid m) \), \( \text{cn}(v \mid m) \), \( \text{dn}(v \mid m) \), and \( \text{cd}(v \mid m) \) are Jacobian elliptic functions of argument \( v \) and parameter \( m \) in standard notation, at \( v = \mathcal{H} / \mathcal{H} \mathcal{G}[\mathcal{G}[m] / 2] \) and \( m = \exp(2\mathcal{G}[\mathcal{G}[m] \) . The above procedure yields the electrostatic interaction with the surface chemical equilibrium maintained at all particle separations, i.e., full charge regulation (Behrens et al., 2000).

When the surface potential is low \( (\mathcal{G}_0 < 25 \text{ mV}) \), the Poisson-Boltzmann equation may be replaced by its linearized version, the Debye-Huckel equation. The pair interaction energy then has the analytical form:

\[ V(h) = 2\mathcal{R} \mathcal{G}_b (\mathcal{G}_0)^2 \prod \ln[1 + \mathcal{G}(\mathcal{G}[h])] \quad (2.9.7) \]

with \( \mathcal{G} = (C_{\text{reg}} + C_{\text{at}})/(C_{\text{reg}} + C_{\text{at}}) \) taking values between \(-1 \) and \( 1 \) depending on the ability of the surfaces to adjust their charge density upon approach (Behrens et al., 2000)
2.9.2 Van der Waals
Van der Waals forces are present between all colloidal particles. Many physical phenomena are consequence of these forces. Examples include: the behavior of real gases, surface tension of liquids, adsorption of gases on solids and aggregation of colloidal particles. These forces arise from spontaneous electrical and magnetic polarizations, giving a fluctuating electromagnetic field within the media and in the gap between them.

Van der Waals forces have several components that correspond to different molecular interactions, but the most relevant are (Marquez, 1994):

1) Debye or Induction interaction which results from the attraction of permanent and induced dipoles.

2) Keesom or dipole orientation that acts between permanent dipoles.

3) London or dispersion energy between induced dipoles.

There are two approaches to deriving van der Waals forces: (1) the classical (microscopic) approach, and (2) the macroscopic approach. The classical approach is due to Hamaker (1937), the interaction between 2 macroscopic bodies is obtained by the summation of all the relevant intermolecular interactions (Elimelech et al., 1995).

2.9.2.1 Hamaker Expressions for Interacting Spheres
The Hamaker expressions are based the assumption of pairwise additivity of intermolecular forces. The interaction between two particles is calculated by summing the interactions of all molecules in one particle with all of the molecules in the other (Elimelech et al., 1995). Each van der Waals expression can be split into a geometrical part and a constant A, the Hamaker constant, which is related only to the properties of the interacting macroscopic bodies and the medium. A is usually in the range of $10^{21}$ J to $10^{19}$ J (Elimelech et al., 1995). Assuming that two equal spheres of radius $a_1$ are immersed in a vacuum, the result is given by:
\[ V_A = -\frac{A_1 a_1}{12h} \]  

(2.9.8)

These expressions apply at close approach, and become quite inaccurate at separations greater than 10% of the particle radius (Elimelech et al., 1995). In many cases the interaction energy is negligible at larger distance so that equations like the one above are acceptable for practical purposes. For interaction of media through a liquid the same expressions can be used, but with a modified Hamaker constant. A useful approximation for Hamaker constants of different media is the geometrical mean assumption:

\[ A_{12} = (A_{11}A_{22})^{1/2} \]  

(2.9.9)

2.9.3 Other Interparticle Forces
There are situations where two principle forces alone (double layer and van der Waals interactions) does not give satisfactory agreement with experimental results. For colloidal particles carrying adsorbed polymers, the forces are steric or osmotic forces.

The presence of an adsorbed layer can sometimes have a significant influence on the stability of colloidal dispersions through one or more of the following mechanisms:

1. by changing the electrical double layer force either directly, in the case of polyelectrolytes or by causing a displacement of the Stern surface

2. by altering the interparticle van der Waals attraction by modifying the effective Hamaker constant

3. by generating additional interactions either due to desorption of adsorbed molecules, or compression and interpenetration of adsorbed layers.

2.9.3.1 Born Repulsion
This short-range repulsion (within 1 nm) originates from the strong repulsive forces between atoms as their electron shells interpenetrate each other. A precise description of the interatomic structure must be based on quantum mechanical considerations. However, a
number of simplified approximate equations have been proposed, and of these, the most widely used is the Lennard-Jones m-n potential:

\[ V_{LJ} = 4\epsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \]  

(2.9.10)

where \( r \) is the interatomic separation, \( \sigma \) the collision diameter, and \( \epsilon \) the depth of the primary energy well. The attractive part is due to van der Waals interaction and the repulsive contribution is known as Born repulsion.

2.9.3.2 Steric Interaction

Adsorbed layers can play a very important role in aggregation phenomena. In the case of colloidal particulate dispersions with larger adsorbed amounts, polymers can give great stability, by an effect known as steric stabilization. The stabilizing action of such materials can be interpreted in simple terms. As particles approach sufficiently close, the adsorbed layers come into contact and any closer approach would involve some interpretation of the hydrophilic chains. Since these chains are hydrated, overlap of these layers would cause some dehydration and an increase in free energy and a repulsion between particles. For an initial approximation, the repulsion can be assumed to become infinite as soon as the adsorbed layers begin to overlap, but zero at greater separations.

2.10 Population Balances

Population balance models are used in situations where large numbers of entities need to be tracked and modified in the course of simulation. For this reason, population balance models have historically been used in studies of crystallization, aerosol dynamics, comminution, heterogeneous phases, protein precipitation, latex reactors, and particulate systems.

Even though the concept of continuity can be extended to heterogeneous systems, many times the mathematical description cannot. Continuous formulation of a population balance for aggregation produced in a suspension can be formulated as a system of partial
integro-differential equations, but the solution of such a solution is difficult numerically. Hounslow (1988) proposed a general approach to circumvent this difficulty. He proposed a general population balance in discrete form that can be expressed as a set of differential equations as opposed to a system of Partial-Integro-Differential equations (PID) for continuous population balances (Marquez, 1994). The discrete population balance (DPB) introduces the discretization at the formulation stage rather than discretize a continuous formulation (Marquez, 1994).

There are three significant drawbacks to the use of population balances. The first drawback is the numerical difficulty involved with using the PIDs, which result from using population balances. The second drawback is that boundary conditions have to be known and set before a solution can be attempted. The third drawback is that population balance models sometimes may agree with certain experimental sets, but do not represent the true fundamentals of the system under study (Fisher, 1998).

Consider a distribution of entities, \( \mathbf{\Omega} \), distributed throughout an arbitrary region of dimensional space (xyz) known as \( V' \), and through some region \( R' \) of property space, \( \mathbf{\Omega}_m' \):

\[
\mathbf{\Omega} = \mathbf{\Omega}(x, y, z, \mathbf{\Omega}_1', \mathbf{\Omega}_2', ..., \mathbf{\Omega}_m', t) \tag{2.10.1}
\]

where \( x, y, z \) are spatial coordinates, and \( \mathbf{\Omega}_1', \mathbf{\Omega}_2', ..., \mathbf{\Omega}_m' \) represent property coordinates over which the entities are distributed. (Fisher, 1998). The property coordinates could represent size, age, or composition of particles (Marquez, 1994). One way of looking at the point population density function, \( \mathbf{\Omega} \), over \( V' \) and \( R' \) is that:

\[
\frac{\mathbf{\Omega} dR'V'}{\int_{R'=V'} \mathbf{\Omega} dR'V'} \tag{2.10.2}
\]

is the fractional portion of the total population distribution which find themselves in the regions \( x \) to \( x + dx \), \( y \) to \( y + dy \), \( z \) to \( z + dz \), \( \mathbf{\Omega}_1 \) to \( \mathbf{\Omega}_1 + d\mathbf{\Omega}_1 \), ..., \( \mathbf{\Omega}_n \) to \( \mathbf{\Omega}_n + d\mathbf{\Omega}_n \). It is
assumed that the various components of the spatial and property regions \( R' \) and \( V' \) are continuous in nature and the propagation of these spatial coordinates and properties can be defined as \( ve_x, ve_y, ve_z, ve_1, ve_2, \ldots, ve_m \), where:

\[
ve_1 = \frac{d[n]}{dt}
\]  

(2.10.3)

Continuing, it is necessary to define a manner in which to modify the number density distribution \[.\]. This manner of modification is through the birth and death functions operating through the space and property region \( V' \) and \( R' \). The birth function is the number of entities created at a point \( V' \) and \( R' \) is:

\[
B = B(x, y, z, \square_1, \square_2, \ldots, \square_n, t)
\]  

(2.10.4)

The units of the birth term are entities per volume per second per unit property entities. The death function is the number of entities destroyed at a point in \( V' \) and \( R' \) is:

\[
D = D(x, y, z, \square_1, \square_2, \ldots, \square_n, t)
\]  

(2.10.5)

The birth and death functions are point functions of the state of the system. The birth and death functions are governed by the physical state of the system, and are used to characterize conditions with the changing number distribution \[.\] (Fisher, 1998).

Let us redefine the combined regional and property space, \( P \), as the particle state vector, which consists of both \( R' \) and \( V' \). The conservation relationship is:

\[
\text{Accumulation} = \text{Input - Output + Net Generation}
\]  

(2.10.6)

In terms of the nomenclature defined above:

\[
\frac{d}{dt} \bigg( \bigwedge_P dP \bigg) = \bigwedge_P B_1 \bigwedge D_1 dP + \bigwedge_P B_2 \bigwedge D_2 dP + \ldots + \bigwedge_P B_n \bigwedge D_n dP
\]  

(2.10.7)
where $dP = dxdydz d\Theta_1 d\Theta_2 ... d\Theta_m$

The last equation can be expanded to:

$$\frac{d}{dt} \left[ \prod P dP \right] = \frac{d}{dt} \left[ \prod x y z \prod \right] ... \prod d\Theta_m d\Theta_1 d\Theta_i dz dy dx \quad (2.10.8)$$

This equation can be expanded further to a more useful term by repeatedly differentiating inside the integrals using the general rule of Leibnitz. The equation now becomes:

$$\prod \frac{\partial T}{\partial t} + \prod \frac{\partial}{\partial x} (ve_x, \prod) + \prod \frac{\partial}{\partial y} (ve_y, \prod) + \prod \frac{\partial}{\partial z} (ve_z, \prod) + \prod m \frac{\partial}{\partial \Theta_i} (ve_i, \prod) + D \prod B \prod dP = 0 \quad (2.10.9)$$

Considering that the region P was arbitrarily defined, it is more compact to rewrite the equation in vector notation:

$$\frac{\partial \prod}{\partial t} + \prod \cdot (\bar{v} \bar{e}) + \prod m \frac{\partial}{\partial \Theta_i} (ve_i, \prod) + D \prod B = 0 \quad (2.10.10)$$

where the vector $ve$ is the average velocity vector of the particles in the spatial region $V'$.

The third term in the equation does not show an absolute conservation in accordance with their definitions as properties. However, the combination of the third term with the birth and death terms can be considered much like a source and sink for entity properties. Figure 2.13 (Biggs, 2000) shows a pictorial representation of population balance modeling.
2.11 Aggregate Structure

In the simplest case of equal spheres, a pair of particles would form a dumbbell. A third particle can attach in several different ways, and the greater number of aggregates, the number of possible structures rapidly increases. Figure 2.14 (Elimelech, 1995) shows different particle configurations for an increasing number of primary particles. In most aggregative processes, the number of particles within a particle cluster may be on the order of hundreds or thousands, therefore, an understanding of the nature of the cluster structure is important.
Aggregates are recognized as fractal objects. Fractal aggregates will be discussed in detail in the next few sections.

2.11.1 Fractal Geometry

Euclidean geometry is primarily the study of straight lines and smooth curves. In nature, (the earth) straight lines and smooth curves are the exception rather than the rule. Rugged profiles exist everywhere, from the clouds in the sky, to the outlines of trees and mountain ranges, and the stars in the sky. Fractals are characterized by a non-integer power law dependence of a measurable quantity upon the length of the object (or upon time) (Mandelbrot, 1983).

The areas and perimeters of fractals are infinite. The farther one zooms in on the perimeter of a fractal, the more bumps, curves, folds, spikes, and curls you see. Mandelbrot (1983) argued that in cases such as this, the exponent can and should be interpreted as a dimensionality.

To simplify this concept, consider the Koch curve (Mandelbrot, 1983). The steps shown in generating a Koch curve are shown in Figure 2.15 (Shabarshin, 2002). One begins with a straight line shown at n = 0 in the figure, known as the initiator. Each section is then
replaced by decisive element defined on the figure as n = 1. The straight-line sections of the first generation curve are then replaced by copies of the generator, and have been shrunk by a factor of three. Four copies are required, leading to the second-generation prefractal curve shown at n = 2. The operation is repeated *ad infinitum*, replacing straight sections by copies of the generator, scaled down by a factor of three with every succeeding generation.

Figure 2.15. Construction Process of the Prefractal Koch Curves

The Koch curve is the limiting curve generated as n → ∞. It is easy to see that the topological dimension of all generations of the prefractal Koch curves (and by extension of the Koch curve also) is equal to one. This is done by setting <h> = w^0 where the exponent \[ is between 0 and 1 (Russ, 1994). The fractal dimension can be calculated, and the rougher values corresponding to the smaller values of \[ have higher fractal dimensions. The quantitative relationship is D = 2 - \[ (Russ, 1994).

2.11.2 Fractal mass scaling
The first scaling feature of aggregates that received wide attention in literature, and the one that remains of great interest to those attempting to characterize aggregation is the mass (or
number) scaling (Bushell, 1998). For a large number of aggregates, the mass is plotted against aggregate size, the plot may be linear, but with a non-integer slope. For aggregates, the slope of the line \( d_f \) is called a mass fractal dimension. The lower the fractal dimension, the more open the aggregate structure. The relationship between aggregate mass, \( M \), and linear measure of size, \( R \), is:

\[
M \propto R^{d_f}
\]  

(2.11.1)

The mass fractal dimension can range between 1 and 3, 3 being the ideal situation of coalescing liquid drops (Elimelech, 1995). Figure 2.17 shows a three-dimensional representation of several aggregates with a fractal dimension ranging from 1.5 to 2.5 (Bushell, 1998). Figure 2.18 (Fisher, 1998) shows the relationship between the coalescence model and the fractal aggregate model for various values of \( D_r \) with a beginning porosity of zero, which would relate to the situation of aggregation from a monodispersed original population (Fisher, 1998). As the figure shows, the relatively loosely packed fractal aggregates that the effective aggregate radius is greatly increases. If the relationship in the above equation applies over a wide range of aggregate sizes, then this implies that aggregates have a self-similar structure, which is independent of the scale of observation. The self-similar structure means that a “small part of the fractal contains information about the whole” (Shabashin, 2002). This concept is illustrated in the Figure 2.16 (Elimelech, 1995) below, where the fundamental unit is assumed to be a triplet of equal spheres.
The essence of self-similar aggregates is that there is a continuum of ‘levels’ from large-scale structures down to individual primary particles.

Early studies on aggregation were based only on the random addition of single particles to growing clusters. These gave fairly dense structures with $d_F$ of about 2.5 (Elimelech, 1995). The early studies were not realistic because single-particle addition does not occur in nature. In reality, aggregation occurs as a result of cluster-cluster encounters. Computer simulations and experimental studies on a range of model colloids show much more open structures with a fractal dimension of about 1.8 (Lin et al., 1989). These simulations assume that particles attach permanently to other particles at first contact; the process is called ‘diffusion-limited aggregation’ (DLA).
Figure 2.17. 3-D Representation of Several Aggregates with $D_t = 1.5 - 2.5$
Figure 2.18. Comparison between the Coalescence and Fractal Aggregate Model

Equation 2.11.1 can take on two subtly different meanings without losing its validity. The first meaning is the scaling of the mass (number of particles) contained within aggregates of different sizes within a cluster polydisperse aggregating system. As a consequence of the (identical) fractal structure of the aggregates, the mass of each aggregate is related to its linear size by the equation. The second meaning is in terms of the structure within any individual aggregate. If we pick an arbitrary particle within an aggregate and center an imaginary sphere upon it, the number of other particles enclosed within the imaginary sphere is related to the linear size of the sphere, $R$, by the last equation. This relationship is only asymptotically correct in the limit of large aggregates and is quite inaccurate for aggregates of only a few particles. To be a bit more specific about the first meaning of equation, it is often written as:
\[ N = k_g \frac{R_g}{r_0}^{\nu} \]  

(2.11.2)

where \( R_g \) is the radius of gyration of the aggregate, \( r_0 \) is the radius of the primary particles and \( k_g \) is known as the power law prefactor (Bushell, 1998). The subscript \( g \) is added to the power law prefactor to clearly associate it with linear aggregate size defined in terms of the radius of gyration, which is the root-mean-square distance of the mass elements from their center of mass.

Real processes that form natural fractals probably impose even more strict limitations on the range of possible fractal dimensions. A simple computer simulation of colloidal aggregation that has been extensively studied is the cluster-cluster aggregation model. This type of simulation allows particles and clusters to diffuse according to specified trajectory (usually Brownian or linear) and stick irreversibly with no restructuring at their point of contact. This type of simulation imposes natural limits on the resulting fractal dimension such that \( \approx 1.8 \). \( D_f \), \( \approx 2.1 \). The lower value comes about when a collision between clusters always results in the formation of a bond. This is known as the diffusion-limited cluster aggregation or DLCA limit and produces quite tenuous, wispy structures. The higher value is a result of collisions almost never forming bonds, so that all physically possible conformations between clusters have an equal chance of forming a bond and thus a new aggregate. This is known as the reaction-limited cluster aggregation or RLCA limit and produces structures that are still quite tenuous and rugged but noticeably more compact and stronger-looking than DLCA aggregates (Bushell, 1998). Despite the simplistic algorithm, there is good evidence that this type of model describes quite accurately a range of colloidal aggregates that can be observed in the laboratory. Thouy and Jullien (1996) reported that their cluster-cluster aggregation model with fractal dimension as a tunable parameter could not produce structures with a fractal dimension higher than about 2.55 in 3-D space because the geometry of the clusters prevented them being placed close enough together to produce higher fractal dimensions.
2.11.3 Packing Density
An interesting consequence of fractal mass scaling is that the density of the fractal object is
not constant as is usually considered the case for everyday solid structures. The mass of the
object is given by the last equation. One way of defining the volume of the object is the
volume of the smallest sphere (radius \( R_e \)) that encloses the structure. This bulk volume is
simply \( 4/3! R_e^3 \). The packing density is given by the aggregate mass divided by bulk
volume (Bushell, 1998):

\[
\mu \frac{R^{D_f}}{R_e^3} = R_e^{D_f/3}
\]  

(2.11.3)

2.11.4 Coordination Numbers
The mass fractal dimension is far from sufficient for complete characterization of
aggregates. Aggregates of fine particles are not really fractal in the strict sense of the word,
since their fractal scaling is only observed over a finite range of length scales. They can be
called natural fractals (Mandelbrot, 1983). At small scales we observe the non-fractal
subunits of which the aggregate is composed. Here we encounter complexities associated
with the short-range non-fractal order of adjacent particles. Even when the primary
particles are as simple as monodisperse spheres we still have to specify first, and depending
on the purpose at hand possibly second and third coordination shell numbers to adequately
quantify the aggregate structure. The mathematical model does not include coordination
numbers, but it is mentioned to provide more a more thorough explanation of fractal nature.

2.11.5 Fractals in Particle Aggregation
The mass within a distance \( r \) of the surface, or for a three-dimensional particle, within a
radius \( r \) of the center of gravity, increases as \( r^E \) for a solid object, where \( E \) is the Euclidean
dimension of the space (2 for a surface, 3 for a solid). For a fractal structure, the exponent
is less. For a classic diffusion-limited aggregate as defined above, the relationship is mass \( \mu \) \( r^{1.73} \) in 2D, mass \( \mu \) \( r^{2.5} \) in 3D (Russ, 1994).
Changes in the rules for motion of the particles or their sticking probabilities alter the appearance and dimension of the clusters. If the sticking probabilities are altered from 100% to 25%, 5%, and 1% respectively, the cluster becomes progressively more compact, and the mass dimension increases (Russ, 1994).

Measuring the real fractal dimension of the cluster, or surface of the cluster is a difficult problem. It has been proposed that as the sticking probability becomes low, the projection of such a cluster will have a boundary that is fractal. A modification of the aggregation modeling technique is to use weighting function. Each time a random particle reaches a site adjacent to the particle that is already part of the cluster, it is counted, but not necessarily added to the cluster. The number of times a particle must reach a site before one is allowed to stick there is a weighting value that can be adjusted to alter the appearance and dimension of the growing cluster. Larger weight values produce increasingly needle-like dendritic shapes.

2.12 Summary
This chapter has examined the basic theory of aggregation processes in colloidal systems. The nature and definition of colloidal systems, model structure for colloidal particles, the nature of surface charging, and a discussion of interparticle forces were covered in this chapter. The theoretical basis for aggregation includes the topics of Smoluchowski aggregation kinetics, description of collision mechanisms, and the definition of the stability ratios. This section contained the background information that is necessary to understand the theory behind the mathematical model presented in Chapter 3.
CHAPTER 3: MATHEMATICAL MODEL FOR AGGREGATION KINETICS

3.1 Introduction
Chapter 2 presented an overview of the basic topics for modeling aggregation phenomena. The model presented in this chapter can be applied to a variety of aggregation processes, and it focuses on the actual implementation of the ideas presented in Chapter 2. A more detailed description and comparison of the collision mechanisms, interparticle forces, stability ratios, and populations balance model is included in this chapter. The discretization method implemented for the population balance model is also discussed.

3.2 Interparticle Forces
The two major contributors to the interparticle interactions are van der Waals attractive forces and electrostatic repulsion interaction energy. The total interaction energy between the two aggregating particles will be represented by the sum of these two forces, which can be expressed mathematically as:

$$V_T(H) = V_R(H) + V_A(H)$$  \hspace{1cm} (3.2.1)

Where $V_T$ is the total interaction energy for the calculation of the stability ratio, $V_R$ is the electrostatic repulsive interaction energy, and $V_A$ is the van der Waals attractive interaction energy. The accuracy of the stability ratios and the corresponding the aggregation rate constants will be determined by the interparticle forces used for their calculation.

3.2.1 Van der Waals Attractive Interaction Energy
This mathematical model will use the Hamaker theory to model the van der Waals forces. Hamaker obtained the following expressions for the potential energy of attraction resulting
from van der Waals forces for different geometries. Interaction of plates of equal thickness (Marquez, 1994):

\[ V_A(l) = \frac{H}{12l} \left[ \frac{h^2}{l^2} + \frac{1}{1 + 2l} \right] \left[ \frac{2}{1 + 2l} \right] \]

(3.2.2)

where \( H \) is the Hamaker constant for the material, \( l \) is the plate thickness, \( l \) is the plate separation, and \( V_A(l) \) is the attractive potential of different radii.

Hamaker derived the attractive potential energy for equal spheres of radius \( a_1 \) and \( a_2 \) and surface-to-surface distance \( H \) is given by:

\[ V_A(H) = \frac{A}{6} \left[ \frac{2a_1a_2}{h^2 + 2a_1h + 2a_2h} + \frac{2a_1a_2}{h^2 + 2a_1h + 2a_2h + 4a_1a_2} + \ln \left( \frac{h^2 + 2a_1h + 2a_2h}{h^2 + 2a_1h + 2a_2h + 4a_1a_2} \right) \right] \]

(3.2.3)

where \( h = \frac{d_1 + d_2}{2} + s \) is the distance between the particle center, and \( s \) is the separation distance between surfaces as shown in Figure 3.1 (Ahmadi, 2001). The assumption of complete additivity is a serious deficiency and the resulting expressions always overestimate the interaction.

![Figure 3.1. Contact of Two Dissimilar Spheres](image-url)
Figure 3.2 shows the potential energy of interaction between particles of dissimilar radii (Fisher, 1998). The x-axis of the graph shows the particle separation, while the y-axis shows the radius of one of the particles while the other is held constant at 100 nm. As the particle mismatch becomes greater, the interaction energy tends to saturate while the interaction is dominated by the larger particle. Figures 3.3 shows the interaction energy as a function of particle surface separation. Figure 3.4 shows the interaction energy as a function of particle diameter.

Figure 3.2. Potential Energy of Interaction for Different Particle Sizes
Figure 3.3. Potential Energy of Attraction for Different Particle Sizes

Figure 3.4. Potential Energy of Attraction for Different Particle Sizes
3.2.2 Electrostatic Repulsion Interaction Energy

In order to calculate the interaction energy between two particles due to the overlap of their double layers, it is necessary to know the electrostatic potential profile that develops between the interacting particles. This is accomplished with the Poisson-Boltzmann equation (PBE), which was introduced in Chapter 2. Solution of PBE will yield the electrostatic potential profile between two surfaces for the given boundary conditions. Adequate integration of the electrostatic potential will provide the repulsive potential energy between the interacting surfaces. Unfortunately, the PBE does not have an analytical exact solution for even the simplest system of two plates with constant surface potentials. Analytical solutions to the Poisson-Boltzmann equation are only available for certain values of the surface potential and double-layer thickness (Fisher, 1998). Fortunately, aggregation processes are conducted within the range where these analytical values are valid.

The interaction energy is calculated in two different ways in the mathematical model: linearized Poisson-Boltzmann equation, and the non-linearized Poisson-Boltzmann equation. Figures 3.5 and 3.6 show the potential energy of repulsion for different particle sizes with the linearized Poisson-Boltzmann equation, which is described in Section 3.2.2.1.
Figure 3.5. Potential Energy of Repulsion for Different Particle Sizes

Figure 3.6. Potential Energy of Repulsion for Different Particle Sizes
3.2.2.1 Linearized PBE

The linearized Poisson-Boltzmann equation is based on the solution of Hogg, Healy, and Fuerstenau (Hogg et al., 1966), and provides a solution for the electrostatic interaction energy between two dissimilar sphere and unequal surface potentials (Fisher, 1998):

$$ V_k(H) = \frac{a_1 a_2 (\frac{\bar{a}^2}{a_1^2} + \frac{\bar{a}^2}{a_2^2})}{4(a_1 + a_2)} \ln \frac{1 + \exp(\bar{a}H)}{1 \exp(\bar{a}H)} + \ln(1 \exp(\bar{a}H)) $$

(3.2.4)

This expression is limited to $\bar{a} \geq 5$, and values of the surface potentials up to 70 mV (Fisher, 1988). This form of the electrostatic interaction energy equation will be abbreviated HHF from now on.

3.2.2.2 Non-linear PBE

The non-linear PBE form of electrostatic repulsion will be used when the solution and system parameters are not within the range of the HHF solution. The original algorithm was based upon the work of Chan, Pashley, and White (1980). This algorithm has several disadvantages such as the fact that it was valid only for identically charged surfaces, where the electrostatic potential goes through a midpoint between plates (Fisher, 1998). This method was improved by Marquez (1994), and is based on the numerical solution using the Rutta-Kutta integration of the Poisson-Boltzmann equation for the flat plate coupled with the method of Papadopoulos and Cheh (1984). A quick overview of the method of Papadopoulos and Cheh (1984) is presented below.

Papadopoulos and Cheh (1984) solved the linearized Poisson-Boltzmann equation using a modified form of Derjaguin’s approximation. A similar system of rings was used to represent the spherical surfaces of particles, but instead of using the shortest distance between plates, they considered them separated by a distance equal to the arc of a circle perpendicular to both rings. For two spheres of radii $a_1$ and $a_2$, they obtain the following expression:
\[ V_R(H) = \int_0^{\theta_{\text{max}}} Y_f(s) \sin \theta \, d\theta + \int_0^{\theta_{\text{max}}} Y_f \sin \theta \, d\theta \tag{3.2.5} \]

where \( V_f \) is the interaction energy per unit area of two parallel plates separated by a distance equal to the length of the arc of a circle, \( s \), perpendicular to both rings. \( \theta_{\text{max}} \) and \( \theta_{\text{max}} \) are represented by:

\[ \theta_{\text{max}} + \theta_{\text{max}} = \theta \tag{3.2.6} \]

\[ s = \frac{\theta + \theta}{2 \sin \theta} - \frac{2a_i^2 \sin^2 \theta}{\cos^2 \theta} + \frac{a_i^2 \theta}{R} - \frac{2a_i \theta}{\cos \theta} \tag{3.2.7} \]

A graphical representation is shown in Figure 3.7 (Marquez, 1994).

![Graphical Depiction of the Method of Papadopoulos and Cheh](image_url)

Figure 3.7. Graphical Depiction of the Method of Papadopoulos and Cheh

Marquez (1994) used exact numerical solutions based on a method of collocation of finite elements instead of the linearized form of the Poisson-Boltzmann equation for flat plates (Fisher, 1998). A quick overview of the derivation of the formula is presented below. For a more detailed discussion of the non-linear PBE, refer to Appendix A.
The derivation starts with a dimensionless form of the Poisson-Boltzmann equation in one dimension:

\[
\frac{d^2\phi}{dy^2} = \phi^2 \sinh(\phi) \quad (3.2.8)
\]

where \( \phi \) is the dimensionless surface potential, and \( y \) is the distance from the origin. The boundary conditions for the case of a constant surface potential (Fisher, 1998):

\[
\phi(0) = \phi_1 \quad \phi(X_d) = \phi_2 \quad (3.2.9)
\]

where \( X_d \) is the separation between plates. Integrating equation gives:

\[
\int \frac{d\phi}{dx} \sqrt{\phi} = 2 \cosh(\phi) + C \quad (3.2.10)
\]

where \( C \) is an unknown integration constant and \( x = \frac{y}{\phi} \). If \( \phi \) has a minimum \( \phi_{\text{min}} \) the value of the integration constant is (Fisher, 1998):

\[
C = \phi_2 \cosh(\phi_{\text{min}}) \quad (3.2.11)
\]

The last equation is solved with the boundary conditions for both the monotonic and concave case. The limitation on the solution is that \( \phi_1 > \phi_2 > 0 \).

For every value of \( C \) there is a distance between the plates given by (Fisher, 1998):

\[
X_d = \phi_1 \frac{d\phi}{\sqrt{2 \cosh(\phi) + C}} + \phi_2 \frac{d\phi}{\sqrt{2 \cosh(\phi) + C}} \quad (3.2.12)
\]

if \( \phi \) has a minimum and by \( \frac{\phi_1}{\sqrt{2 \cosh(\phi) + C}} \) if \( \phi \) is monotonic.
Let $x_{ref}$ be the distance between the plates resultant to a particular case in which (Fisher, 1998):

$$\frac{d\square}{dx}(\square_2) = 0 \quad \text{With} \quad \square_{\min} = \square_2$$

(3.2.13)

Which can be thought of as $\square$ reaching a minimum exactly at the boundary condition. In order to compute $X_d$ for the monotonic case, the following differential equation needs to be integrated:

$$\frac{d\square}{dx} = \sqrt{2 \cosh(\square)} + C \quad \square(0) = \square_1$$

(3.2.14)

until $|\square - \square_2| < \text{TOL}$, while in the convex case the next two differential equations have to be integrated:

$$\frac{d\square}{dx} = \sqrt{2 \cosh(\square)} + C \quad \square(0) = \square_1$$

(3.2.15)

until $|d\square/dx| < \text{TOL}$ and $\frac{d\square}{dx} = \sqrt{2 \cosh(\square)} + C$ until $|\square - \square_2| < \text{TOL}$. TOL is a small value that is chosen as the limit of accuracy to which the computations are conducted (Fisher, 1998).

In both cases $C$ has to be determined using a search algorithm until the separation between plated corresponding to the integration chosen matches within a given tolerance the separation between the sets set by the problem (Fisher, 1998). The following limits are used:

Concave Case: $-2\cosh(\square_2) \begin{array}{cc} \square \end{array} C \begin{array}{cc} \square \end{array} -2$

(3.2.16)

Monotonic Case: $-2\cosh(\square_2) \begin{array}{cc} \square \end{array} C \begin{array}{cc} \square \end{array} 10\cosh(\square_1)$

(3.2.17)
The selection of these limits is discussed in Appendix 2 (Fisher, 1998). The limit for the monotonic case is selected on the basis of the highest potentials and the shortest distances most likely encountered (in actuality the upper limit is infinity) (Fisher, 1998).

The numerical integration method that is used is Runge-Kutta-Fehlberg with error control (Burder and Faires, 1985), while the search algorithm for the integration constant C is Brent’s algorithm (Press et al., 1984). A flowsheet of the entire method is presented in Figure 3.8 (Marquez, 1994).
Input $X_d$, $\psi_1$, $\psi_2$

$C = -2\cosh(\psi_2)$

Integrate equation 3.2.14 representation by RKF monotonically to get $x_\text{ref}$

$C_{\text{min}} = C$
$C_{\text{max}} = 10\cosh(\psi_1)$
$x_{\text{max}} = 5$
$TOL = 1.0e-6$
$er = 10$

$x_{\text{max}} < x_{\text{ref}}$

$c_r = -2.0$
$c_l = c_{\text{min}}$

While $er > TOL$

Compute next $C$ using Bisection

Integrate equation 3.2.14 by RKF for concave case to get $x_c$

$X_c > x_{\text{max}}$

$c_r = C$
$c_r = C$
$er = x_{\text{max}} - x_c$
$C_{\text{max}} = C$

While $er > TOL$

Compute next $C$ using Bisection

Integrate equation 3.2.14 by RKF for concave case to get $x_c$

$X_c > x_{\text{max}}$

$c_r = C$
$c_r = C$
$er = x_{\text{max}} - x_c$
$C_{\text{max}} = C$

$er = 10.0$

Continue to next page
figure 3.8. Flowsheet for Numerical Integration of Non-Linear PBE
3.2.2.3 Comparison of Linear and Non-linear PBE

This section will investigate the range of applicability for the linear and non-linear PBE. Three different solutions will be compared:

1. OHW: Deraguin’s integration with series approximation presented by Ohima, Healy, and White (Ohshima et al., 1994).


3. PRKF: Papadopoulos integration with numerical solution.

The results are plotted with dimensionless distance as the x-axis, and the dimensionless potential as the y-axis. The dimensionless distance is the particle surface-to-surface separation, $H$, times the double-layer thickness, $\bar{d}$. The dimensionless potential is the potential divided by $kT$, where $k$ is the Boltzmann constant and $T$ is the absolute temperature. These dimensionless groups are used so that comparisons can be made without taking into account the effects of ionic concentration.

HHF has little loss of accuracy if the values of both surface potentials are low, and the double-layer thickness ($\bar{d}$) is greater than or equal to 5. When surface potentials are large, or the particle sizes are small, the method of Papadopoulos makes a significant difference. The Papadopoulos technique is needed for smaller particles. Figure 3.9 shows the variation between HHF and Papadopoulos with larger surface potentials. Figures 3.10 – 3.12 show examples under which the HHF approximation can be used with little loss of accuracy. Figure 3.13 shows both equal and unequal small particle sizes as well as equal and unequal low surface potentials with the linear and non-linear forms of the Poisson-Boltzmann equation.
Figure 3.9. PBE Interaction Energy Comparison
Figure 3.10. PBE Interaction Energy Comparison
Figure 3.11. PBE Interaction Energy Comparison
Figure 3.12. PBE Interaction Energy Comparison
3.3 Collision Mechanisms
The three collision mechanisms that were presented in Chapter 2 are: perikinet, orthokinetic, and sedimentation. They are summarized below:

Perikinet:
\[ k_{ij} = \frac{2kT}{3} \left( a_i + a_j \right)^2 \]  
(3.3.1)

Orthokinetic:
\[ k_{ij} = \frac{4}{3} G (a_i + a_j)^3 \]  
(3.3.2)

Differential Settling:
\[ k_{ij} = \frac{2G}{9} \left( a_i + a_j \right)^3 (a_i + a_j) \]  
(3.3.3)
Figures 3.13 through Figures 3.15 shown the general form for the three collision mechanisms. All of these figures used the case of polystyrene in water at 25 °C for demonstration purposes. Figure 3.13 shows the perikinetic rate constant as a function of particle size. From equation 3.3.1, it is apparent that the aggregation rate constant for the perikinetic case varies proportionally with temperature and inverse proportionally to solvent viscosity.

![Perikinetic Rate Constant for Aggregation](image)

**Figure 3.14. Perikinetic Rate Constants**

Figure 3.15 shows the orthokinetic case as a function of particle size for a shear rate of 50 s⁻¹. If equation 3.3.2 is examined, it is obvious that the aggregation rate constant varies proportionally with average shear rate G.
Figure 3.15. Orthokinetic Rate Constants

Figure 3.16 shows the differential settling rate constants as a function of particle size with a particle density of 2.5 g/cm³. This figure demonstrated that the aggregation rate constant approaches zero for particles of the same size. Equation 3.3.3 shows that the rate is inversely proportional to the solvent viscosity, and varies proportionally to the difference of particle density and solution density.
Figure 3.16. Differential Settling Rate Constants

The differential settling collision mechanism will not be used in the experiments conducted with the mathematical model because of the range of particle sizes is $10^{-9}$ m (10 Å) to 9 * $10^{-6}$ m (1 μm) in size. The differential settling collision mechanism is primarily used for particle sizes of 100 microns and above.

3.4 Stability Ratios
The stability ratios discussed in Chapter 2 are summarized below:

**Perikinetic:**

$$ W = 2 \int_{0}^{\infty} \frac{\exp(\frac{d}{u} / kT)}{(u + 2)^{2}} \, du $$

**Orthokinetic:**

$$ \left( \ln\left(\frac{d}{2a}\right) \right)^{29} \frac{d^{0.075}}{2a^{0.2}} \right)^{3/2} $$

(3.3.4)
3.4.1 Perikinetic Stability Ratios

The integration of the stability ratios for the perikinetic collision mechanism is computationally difficult in two ways: (1) the limits to which the integration must be carried out, and (2) the general form of the integrand. The limits of integration cover the range from particle contact to infinity. Traditional techniques such as the trapezoidal rule would require many integration steps to cover the entire range of integration (Fisher, 1998).

To decrease the computational time, and still maintain a high degree of accuracy, Gaussian quadrature is used. Breaking up the range into many subintervals using a geometric distribution can also increase the computational efficiency. The function will be integrated as follows:

$$\int_{a}^{b} f(x)dx = \sum_{i=1}^{L} \int_{a}^{a+h} f(x)dx$$

where $L_i = a + h \sum_{j=0}^{i} r_g^j$ (3.3.6)

$r_g$ is the geometric ratio used to increase the size of the intervals progressively. Each subinterval uses Gaussian quadrature to increase computational accuracy.

Figures 3.17 and 3.18 show a map of the stability ratios calculated using the HHF approximation and the RKF numerical integration solution for the Poisson-Boltzmann equation respectively. For these examples, polystyrene in water is used again with a 25 mV Zeta potential.
Figure 3.17. Stability Ratios for HHF

Figure 3.18. Stability Ratios for RKF and Papadopoulos
3.4.2 Orthokinetic Stability Ratios

The orthokinetic stability ratios take hydrodynamic forces into account in the calculation of the aggregation coefficients based on the orthokinetic collision mechanism. Figure 3.19 shows the map of stability ratios with a primary particle size of 0.102 microns.

![Stability Ratios for Orthokinetic Collision Mechanism](image)

Figure 3.19. Stability Ratios for Orthokinetic Collision Mechanism
Figure 3.20 shows the map of stability ratios with a primary particle size of 0.155 microns.

![Log of Stability Ratios](image)

**Figure 3.20. Stability Ratios for Orthokinetic Collision Mechanism**

3.5 Map of Aggregation Coefficients

In Chapter 2, the aggregation kernel is defined in terms of the continuous population balance model for aggregation. The aggregation coefficient, $\Pi$, is the rate constant for two particles. The aggregation coefficient is defined as (Fisher, 1998):

$$\Pi_{i,j} = \frac{k_f}{W_{i,j}}$$  \hspace{1cm} (3.4.1)

where $k_f$ is the rate of aggregation derived from the appropriate collision mechanism, and $W_{i,j}$ is the stability ratio calculated from the models for interparticle forces. Figures 3.21 through 3.24 show examples of the final map of aggregation coefficients used in the solution of mathematical model for the corresponding collision mechanism. The rate of aggregation used for this calculation was calculated the Figures 3.14 through 3.16, and the stability ratios were calculated in Figures 3.17 and 3.19. Notice that as the particle size
increases, the rate constant for aggregation decreases, which cause the self-similar size distribution often found in colloidal systems.

Figure 3.21. Log of Aggregation Coefficients for Perikineti Collision Mechanism
Figure 3.22. Log of Aggregation Coefficients for Orthokinetic Collision Mechanism

Figure 3.23. Log of Aggregation Coefficients for Differential Settling Mechanism
3.6 Population Balance Formulation

The population balance equation from Chapter 2 is:

$$\frac{dn(L)}{dt} = B(L) \cdot D(L)$$

(3.5.1)

where the birth and death functions are:

$$B(L) = \frac{L^2}{2} \int_0^L \left( \frac{L^3}{L^3} \right)^{3/3} n \left( \frac{L^3}{L^3} \right)^{1/3} n(dL)$$

(3.5.2)

$$D(L) = n(L) \int_0^L (L, dL)n(dL)$$

(3.5.3)

The discretization of Litster et al. (1995), and Wynn (1996) is used to complete the mathematical model.

3.6.1 Discretization Method

The accuracy of the population balance models are very importance for the modeling of the aggregation process because they are the basis of the mathematical model. The methods of discretion used for this mathematical model are more general in application than other methods such as orthogonal collocation, and rely less on the significant tuning of the algorithms for the different initial distributions and aggregation kernels (Fisher, 1998). The discretization method also is relatively easy to use, therefore, it is an excellent choice for a general mathematical model. Since the discretization method plays an important role in this mathematical model, a derivation of the numerical integration with a thorough error analysis is necessary.

The method of discretization used in this mathematical model was originally proposed by Hounslow (1988, 1990). This method is based upon geometric discretization of the particles in terms of volume or length (Fisher, 1998):
\[
\frac{v_{i+1}}{v_i} = 2 \quad \text{or} \quad \frac{L_{i+1}}{L_i} = 2^{1/3} \quad (3.5.4)
\]

where \( v_i \) is the volume, and \( L_i \) is the length of each discretization bin. Each index \( i \) represents a discrete bin of particle concentration, \( N_i \), which is contained within the range of particle size between \( v_i \) and \( v_{i+1} \). Figure 3.24 shows the discrete bins to cover an arbitrary particle size distribution (Hounslow, 2002). This type of geometric discretization allows a relatively small number of discrete bins to cover a large range of particle sizes (Fisher, 1998).

Figure 3.24. Discrete Bins to Cover a Large Range of Particle Sizes

Hounslow derived the following differential equation which relates the change in particle characterization in each bin, \( N_i \), to the concentrations in surrounding bins and the aggregation coefficient, \( \square \) (Fisher, 1998):

\[
\frac{dN_i}{dt} = \sum_{j \neq i} 2 \frac{N_j}{v_j} N_{i,j} + \frac{1}{2} \sum_{j \neq i} \frac{N_j^2}{v_j^2} \sum_{j \neq i} 2 \frac{N_i N_j}{v_i v_j} \sum_{j \neq i} \frac{N_i N_j}{v_i v_j} \quad (3.5.5)
\]
One main disadvantage of this type of discretization is that the particle size divisions are fixed. Due to this limitation, Litster et al. (1995) has improved on the method by proposing an adjustable discretization method:

\[
\frac{V_{i+1}}{V_i} = 2^{1/q} \quad \text{or} \quad \frac{L_{i+1}}{L_i} = 2^{1/3q}
\]

(3.5.6)

where \(q\) is an integer greater than or equal to one, known as the adjustable discretization parameter. The number of discretization bins for a given particle size domain can be increased by increasing the adjustable parameter. This type of discretization still covers a wide range of particle sizes with fewer discretizing bins than linear discretization, and the fineness of discretization can be customized for comparison with experimental results (Fisher, 1998).

A general development of the derivation of Litster et al. discretization method is presented below. The development starts by defining the basic aggregation events between sets of particles. The event fall into five categories (Fisher, 1998):

Particles are created within the interval with the following events:

Type 1: Some of the interactions give particles in the \(i\)th interval and give some particles smaller than the \(i\)th interval.

Type 2: All interactions give particles in the \(i\)th interval.

Type 3: Some interactions give particles in the \(i\)th interval and some give interactions larger than the \(i\)th interval.

Particles are removed from the interval by the following events:

Type 4: Some interactions remove particles from the \(i\)th interval.

Type 5: All interactions remove particles from the \(i\)th interval.
A summary of interactions is provided in Table 3.1. It is evident which of these interactions fall into the five categories by examining the particle interactions involving particles bounding each interval (Fisher, 1998).

Table 3.1. Table of Aggregation Events for the Method of Litster et al

<table>
<thead>
<tr>
<th>q</th>
<th>Size Interval 1</th>
<th>Type 1 (Birth)</th>
<th>Type 2 (Birth)</th>
<th>Type 3 (Birth)</th>
<th>Type 4 (Death)</th>
<th>Type 5 (Death)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>i</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1 $\times$ j $\times$ i-1</td>
<td>i $\times$ j $\times$</td>
</tr>
<tr>
<td></td>
<td>i-1</td>
<td>1 $\times$ j $\times$ i-2</td>
<td>i-1</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>i</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1 $\times$ j $\times$ i-3</td>
<td>i-2 $\times$ j $\times$</td>
</tr>
<tr>
<td></td>
<td>i-1</td>
<td>1 $\times$ j $\times$ i-4</td>
<td>—</td>
<td>i-3 $\times$ j $\times$ i-2</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>i-2</td>
<td>i-4 $\times$ j $\times$ i-3</td>
<td>i-2</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>3</td>
<td>i</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1 $\times$ j $\times$ i-6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>i-1</td>
<td>1 $\times$ j $\times$ i-7</td>
<td>—</td>
<td>i-6 $\times$ j $\times$ i-4</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>i-2</td>
<td>i-7 $\times$ j $\times$ i-5</td>
<td>—</td>
<td>i-4 $\times$ j $\times$ i-3</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>i-3</td>
<td>i-5 $\times$ j $\times$ i-4</td>
<td>i-3</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>4</td>
<td>i</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1 $\times$ j $\times$ i-10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>i-1</td>
<td>1 $\times$ j $\times$ i-11</td>
<td>—</td>
<td>i-10 $\times$ j $\times$ i-7</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>i-2</td>
<td>i-11 $\times$ j $\times$ i-8</td>
<td>—</td>
<td>i-7 $\times$ j $\times$ i-5</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>i-3</td>
<td>i-8 $\times$ j $\times$ i-6</td>
<td>—</td>
<td>i-5 $\times$ j $\times$ i-4</td>
<td>—</td>
<td>—</td>
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<tr>
<td></td>
<td>i-4</td>
<td>i-6 $\times$ j $\times$ i-5</td>
<td>i-4</td>
<td>—</td>
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<td>—</td>
</tr>
<tr>
<td>q</td>
<td>i</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1 $\times$ j $\times$ S(q)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>i-1</td>
<td>1 $\times$ j $\times$ i-S(q)-1</td>
<td>—</td>
<td>i-S(q) $\times$ j $\times$ i-S(q-1)-1</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>i-2</td>
<td>i-S(q)-1 $\times$ j $\times$ i-S(q-1)-2</td>
<td>—</td>
<td>i-S(q-1)-1 $\times$ j $\times$ i-S(q-2)-2</td>
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<td>—</td>
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<tr>
<td></td>
<td>i-3</td>
<td>i-S(q-1)-2 $\times$ j $\times$ i-S(q-2)-3</td>
<td>—</td>
<td>i-S(q-2)-2 $\times$ j $\times$ i-S(q-3)-3</td>
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<tr>
<td></td>
<td>i-q</td>
<td>i-S(2)-q+1 $\times$ j $\times$ i-S(1)-q</td>
<td>i-q</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>
To understand Table 3.1, the definition of $S(q)$ needs to be explained. $S(q)$ relates the important subintervals which aggregate with interval $q$ to form new particles within the $i$th interval (Fisher, 1998):

$$S(q) = \sum_{j=1}^{q} p$$  \hspace{1cm} (3.5.7)

Inspection of Table 3.1 gives the rate of change for $N_i$, the number concentration in any discretization bin, given any value of $q$ (Fisher, 1998):

$$\frac{dN_i}{dt} = \sum_{j=1}^{q} K_1 \Box_{[j]} N_i N_j + \sum_{k=2}^{q} \frac{1}{2} \Box_{[k]} N_i N_j \hspace{1cm} (3.5.8)$$

$$\frac{dN_i}{dt} = \sum_{k=2}^{q} K_2 \Box_{[k]} N_i N_j + \sum_{j=1}^{q} K_3 \Box_{[j]} N_i N_j + \sum_{j=1}^{q} K_4 \Box_{[j]} N_i N_j + \sum_{j=1}^{q} K_5 \Box_{[j]} N_i N_j \hspace{1cm} (3.5.9)$$

The terms $K_1$, $K_2$, $K_3$, $K_4$, $K_5$ are the fractional portions that are added or removed from the $i$th interval. In the above equations, each term corresponds to a specific aggregation event:

Type 1: First and second terms

Type 2: Third term

Type 3: Fourth term

Type 4: Fifth term

Type 5: Sixth term

In continuing this derivation, Litster et al. follows the same method as presented by Hounslow (1988, 1990) for the case of $q = 1$ for evaluating the K terms (Fisher, 1998). If $v_1 = 2^{1/q}$, the $i$th interval is defined as $2^{i/q} < v < 2^{(i+1)/q}$.

81
The factors $K_1$ and $K_2$ for Type 1 aggregations events will determined using this assumption. The interactions between the particles in the $i$th and $j$th interval where some events give particles in the $i$th interval and give some particles smaller than the $i$th interval. A particle of size between $a$ and $a + da$ must aggregate with a particle in the size range $2^{i+1/q} \cdot a < v < 2^{(i+1)/q}$ from the $i$-th interval to give a particle in the $i$th interval with respect to $a$ is (Fisher, 1998):

$$dR_{|p,j}^{[1]} = \prod_i \prod_p \frac{2^{i(q(p+1))/q} \cdot 2^{i/q} + a}{2^{i(q(p+1))/q} \cdot 2^{i/q} + a} N_i \prod_p \frac{da}{2^{(j+1)/q} \cdot 2^{j/q}} N_j$$ (3.5.10)\n
$$dR_{|p,j}^{[2]} = \prod_i \prod_p N_i \prod_p N_j \frac{2^{i(q(p+1))/q} \cdot (1 \cdot 2^{(j(q+1))/q}) + a \cdot da}{2^{i(q(p+1))/q} \cdot (2^{j/q} \cdot 1)}$$ (3.5.11)\n
The total rate of successful events can be found by integrating this expression between the $i$-th and $j$th intervals (Fisher, 1998):

The values for $K_1$ and $K_2$ are:

$$K_1 = \frac{2^{i/q} + 1}{2^{(i+1)/q} \cdot 1} 2^{i(q(p+1))/q}$$ (3.5.12)\n
$$K_2 = \frac{2^{i/q} \cdot 2^{k/q} \cdot 2^{i+1/q} + 1}{2^{(i+1)/q} \cdot 1} 2^{(j+1)/q}$$ (3.5.13)\n
For the case of Type 2 and Type 5 interactions, all events lead to changes in the $i$th subinterval and are no fractional events. For Type 3 and Type 4 events the values of $K_3$ and $K_4$ must be determined (Fisher, 1998). This is done in a similar manner as the case for Type 1 events and can be found in Appendix 3.

82
Substituting these \( K \) terms into equation yields the following expression for the rate of change of particle number within the \( i \)th discretization bin.

\[
\frac{dN_i}{dt} = \sum_{j=1}^{i[S(q)]} \sum_{j+k}^{i[S(q)]} N_i j \left[ 2^{1/q} \frac{1}{\sqrt{2^{1/q} 1}} + 2^{(j+1)/q} + C_1 \right] \\
+ \sum_{k=2}^{q} \sum_{j=i[S(q)]+1}^{i[S(q)]+k} N_i j \left[ 2^{1/q} \frac{2^{k/q}}{2^{1/q} 1} + 2^{1/q} \frac{1 + 2^{(j+k)/q} + 2^{(j+k)/q}}{2^{(j+k)/q} 1} \right] \\
+ \frac{1}{2} \sum_{k=2}^{q} \sum_{j=i[S(q)]+k+1}^{i[S(q)]+k+2} N_i j \left[ 2^{1/q} \frac{1 + 2^{(j+k)/q} + 2^{(j+k)/q}}{2^{(j+k)/q} 1} \right] \\
+ \sum_{j=i[S(q)]+1}^{i[S(q)]+q} N_i j \left[ 2^{1/q} \frac{1 + 2^{(j+1)/q} + 2^{(j+1)/q}}{2^{(j+1)/q} 1} \right] + C_1 \\
\sum_{j=i[S(q)]}^{i[S(q)]+q} N_i j \\
\sum_{j=i[S(q)]+1}^{i[S(q)]+q} N_i j
\]

(3.5.14)

\( C_1 \) and \( C_2 \) are the volume correction factors. The equation accurately represents the zero moment for any values of \( C_1 \) and \( C_2 \).

The third moment is not predicted as a direct result of the discretization method. Consider a particle in the \( j \)th interval that interacts with a particle in the \( i \)th interval to produce a particle that is still in the \( i \)th interval. Events like this do not affect the number of particles in the \( i \)th interval and are therefore not counted by equation, but for however change the total volume of particulate material present in this interval (Fisher, 1998). In order to account for those interactions which do not affect the zeroth moment, but do not affect other moments in the \( i \)th interval, the inclusion of the correction factors \( C_1 \) and \( C_2 \) is necessary. Appendix 4 shows that the values of \( C_1 \) and \( C_2 \) are:

\[
C_1 = \frac{2^{(j+1)/q}}{2}
\]

(3.5.15)
\[ C_2 = \frac{2^{(j+1)/q}}{2^{1/q} \cdot 1} \left( 2^{1/q} + \frac{1}{2} \right) 2^{(k+1)/q} \cdot 1 + \frac{2^{(k+1)/q}}{2^{1/q} \cdot 1} \]  

(3.5.16)

Combining these volume correction factors with equation yields the following:

\[ \frac{dN_i}{dt} = \sum_{j=1}^{i} \mathcal{S}(q) \cdot \mathcal{D}_{0,i,j} N_{i,j} \cdot 2^{1/q} \cdot 1 \]  

\[ + \sum_{k=2}^{q} \sum_{j=1}^{i} \mathcal{S}(q) \cdot \mathcal{D}_{i,k,j} N_{i,k,1} \cdot 2^{(j+1)/q} \cdot 1 + \frac{2^{(k+1)/q}}{2^{1/q} \cdot 1} \]  

\[ + \frac{1}{2} \sum_{k=1}^{q} \sum_{j=1}^{i} \mathcal{S}(q) \cdot \mathcal{D}_{i,j,k} N_{i,j,k,1} \cdot 2^{(j+1)/q} \cdot 1 \]  

\[ \mathcal{S}(q) \sum_{j=1}^{i} \sum_{k=1}^{q} \mathcal{D}_{i,j,k} N_{i,j,k} \cdot 2^{1/q} \cdot 1 \]  

(3.5.17)

This equation reduces to the original case of Hounslo shown in equation for the case of \( q = 1 \). If \( q \geq 2 \), only two additional summation terms are necessary (Fisher, 1998). This last equation is only correct for cases up to \( q=4 \), but for higher values of \( q \) Wynn (1996) has provided a corrected version of this equation.

In the original work of Litster et al., the summation limits for the differential equation for \( q=1,2,3,4 \), and the general case were assumed by inspection. Wynn provides a more rigorous derivation using the properties of size discretization. The corrected table is shown in Table 3.2.
The derivation for the K terms and the volume correction factors remain unchanged, and only the limits of summation for equation need correction. The function S(q) changes, thus it will not be referred to as S(p). The value of S(p) is not dependent on I, but does depend primarily on q. The corrected function S(p) is given by (Fisher, 1998):

\[
S(p) = \text{Int} \left[ \frac{q \ln(1 - p^{\frac{q}{p-q}})}{\ln 2} \right]^{i-S(q)}
\]  
(3.5.18)

---

Table 3.2. Table of Aggregation Events for the Method of Litster et al (Updated)

<table>
<thead>
<tr>
<th>q</th>
<th>Size Interval 1</th>
<th>Type 1 (Birth)</th>
<th>Type 2 (Birth)</th>
<th>Type 3 (Birth)</th>
<th>Type 4 (Death)</th>
<th>Type 5 (Death)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>i</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1 j i-1</td>
<td>i j j</td>
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<tr>
<td>i-1</td>
<td>1 j i-2</td>
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<tr>
<td>2</td>
<td>i</td>
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<td>—</td>
<td>1 j i-3</td>
<td>i-2 j</td>
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<tr>
<td>i-1</td>
<td>1 j i-4</td>
<td>—</td>
<td>i-3 j i-2</td>
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</tr>
<tr>
<td>i-2</td>
<td>i-4 j i-3</td>
<td>i-2</td>
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<td>3</td>
<td>i</td>
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<td>—</td>
<td>1 j i-6</td>
<td>i-5 j</td>
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<td>i-6 j i-4</td>
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<tr>
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<td>i-7 j i-5</td>
<td>i-4 j i-3</td>
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<td>—</td>
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</tr>
<tr>
<td>i-3</td>
<td>i-5 j i-4</td>
<td>i-3</td>
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<tr>
<td>4</td>
<td>i</td>
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<td>—</td>
<td>1 j i-10</td>
<td>i-9 j</td>
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<td>i-1</td>
<td>1 j i-11</td>
<td>i-10 j i-7</td>
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<td>—</td>
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<tr>
<td>i-2</td>
<td>i-11 j i-8</td>
<td>i-7 j i-5</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>i-3</td>
<td>i-8 j i-6</td>
<td>i-5 j i-4</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>i-4</td>
<td>i-6 j i-5</td>
<td>i-4</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>q</td>
<td>i</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1 j i-S(1)+1</td>
<td>i-S(1)+2 j</td>
</tr>
<tr>
<td>i-p; 1 j p</td>
<td>i-S(p-1)-2 j</td>
<td>i+1-S(p) j</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>q-1</td>
<td>i-S(p)</td>
<td>i+1-S(p+1)</td>
<td>—</td>
<td>—</td>
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<td>.</td>
<td>.</td>
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<td>.</td>
<td>.</td>
</tr>
<tr>
<td>i-q</td>
<td>i-S(q-1) j</td>
<td>i-q</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>i-S(q)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
where \( \text{Int}(x) \) returns the fractional part from \( x \), making it an integer. The corrected number differential for any discretization bin now becomes (Fisher, 1998):

\[
\frac{dN_i}{dt}_{\text{RRS}} = \sum_{j=1}^{1[S]} N_i j N_j \frac{2^{(j[2]+1)/q}}{2^{1/q} 1} \\
+ \sum_{k=2}^{q[S]} \sum_{j=1}^{1[S]} N_i k N_j \frac{2^{(j[2]+1)/q}}{2^{1/q} 1} + 2^{1/q} 2^{1/q} \\
+ \frac{1}{2} \sum_{q[S]} \sum_{j=1}^{1[S]} N_i j^2 N_j \\
\sum_{k=2}^{q[S]} \sum_{j=1}^{1[S]} N_i k N_j \frac{2^{(j[2]+1)/q}}{2^{1/q} 1} + 2^{1/q} 2^{1/q} \\
\sum_{j=1}^{1[S]} \sum_{j=1}^{1[S]} N_i j N_j \\
\sum_{j=1}^{1[S]} \sum_{j=1}^{1[S]} N_i j N_j
\]

In this method of discretization, no integration within subintervals is necessary unlike the methods of Gelbard and Seinfeld (1980) and Landgrebe and Pratsinis (1990). The implementation of the discretization method presented, results in a setoff ordinary differential equations, one differential equation per discretization bin. These differential equations can be evaluated with relative ease, and can be implemented on any personal computer. The current algorithm is implemented with Matlab 5.0 using a Runge-Kutta-Fehlberg integration routine with error control.

3.6.2 Comparison with Analytical Solutions

Analytical solutions to the continuous population balance for aggregation are limited to specialized forms of the initial particle size distribution and aggregation kernels. The comparison will be carried out on the basis of actual number density distribution as a function of time as well as the error in the first six moments of the particle size distribution (PSD). The jth moment of the PSD at any time is given by:
\[ m_j = \int_0^L n(L) dL \]  

(3.5.20)

or in the dimensionless form:

\[ \tilde{m}_j = \left. \frac{m_j}{m_0} \right|_{r=0} = \left. \frac{\int_0^L n(L) dL}{\int_0^L n_0(L) dL} \right|_{r=0} \]  

(3.5.21)

where \( m_j \) is the jth moment of the distribution, \( \tilde{m}_j \) is the dimensionless jth moment of the distribution, \( L \) is the particle length, and \( n(L) \) is the particle number density function (Fisher, 1998). The two cases for comparison will be those of the size independent kernal and the size-dependent sum kernal, both with exponential initial distribution terms of volume. Another term that is useful in graphing and comparing aggregation, is the degree of aggregation, \( I_{\text{agg}} \) which is defined as:

\[ I_{\text{agg}} = 1 \left. \frac{m_0}{m_0} \right|_{r=0} \]  

(3.5.22)

If \( m_0 \) is the total number of particles, the value of the \( I_{\text{agg}} \) ranges from zero to one. In this study, high degrees of aggregation are greater then 0.8, where the total number of particles has been reduced by 80% (Fisher, 1998). Figure 3.25 (Fisher, 1998) shows a comparison for the moments versus \( I_{\text{agg}} \).
3.6.3 Size-Independent Kernal

Gelbard and Sienfeld (1978) provide analytical solutions to the population balance model for aggregation based on the initial distribution:

\[ n_i|_{t=0}(v) = \frac{N_0}{v_0} \exp \left( \frac{v}{v_0} \right) \]  

(3.5.23)

where \( N_0 \) is the total initial number of particles, \( v_0 \) is the initial mean volume. The particle volumes must be converted to length because this is the most common method of viewing particle size distributions. To convert the number density distribution on a volume basis to that of length, or diameter, the following conversion is necessary (Fisher, 1998):

\[ n_D(D, t) = \frac{D^2}{2} n_v(v, t) \]  

(3.5.24)
Gelbard and Sienfeld (1978) present solutions for the size-independent kernel defined as:

$$\Box_0(v_1, v_2) = \Box_0$$  \hspace{1cm} (3.5.25)

where $\Box_0$ is some constant. They present an analytical solution obtained by the method of Laplace Transform (Fisher, 1998):

$$n(v, t) = \frac{4N_0}{v_0(\Box + 2)^2} \exp\left(\frac{2\Box}{\Box + 2}\right)$$ \hspace{1cm} (3.5.26)

where $\Box = N_0\Box t$ is the dimensionless time value, and $\Box = v/v_0$. This equation is referred to as the size-independent (SI) case.

3.6.4 Size-Dependent Kernel
Gelbard and Sienfeld also present solutions for the size-dependent sum kernel defined as:

$$\Box_0(v_1, v_2) = \Box_0(v_1 + v_2)$$ \hspace{1cm} (3.5.27)

where $\Box_0$ is some constant value. An analytical solution is presented by the method of Laplace Transforms (Fisher, 1998):

$$n(v, t) = \frac{N_0(1 \Box T)}{v_0 T^{1/2}} \exp(\Box(1 + T)\Box)I_1(2\Box T^{1/2})$$ \hspace{1cm} (3.5.28)

where $T = 1 - \exp(-\Box)$, $I_1$ is the modified Bessel function of the first kind order one, and $\Box = N_0\Box t$, also known as the dimensionless time value. This equation will now be referred to as the size-dependent (SD) case (Fisher, 1998).

3.6.5 Error Levels in Particle Size Distribution
The levels of error intrinsic in the solution of the population balance for aggregation in comparison with the size-independent and size-dependent case will be investigated in this section. Figures 3.26 and 3.27 show the relative error in moments zero through six for the
SD and SI case for a large value of \( I_{\text{agg}} \) (Fisher, 1998). From these two figures, a reduction in error is shown with increasing \( q \). For the SI case, the value of \( q=1 \), the error in the zero through six moments is less than one percent. The error level for all moments in the SD case is below five percent.

**Figure 3.26. Error in the jth Moment for Size-Dependent Case**
Figure 3.27. Error in the jth Moment for Size-Independent Case

3.7 Mathematical Model Description
All of the ideas and concepts presented in this chapter are put together into a single mathematical model to predict the particle size distribution over a period of time. A map of aggregation coefficients is created to match the discrete bin sizes used in the discretization method. Figure 3.26 shows a flow diagram of the complete mathematical model.
Parameters:
1) Particle Size
2) Boltzmann Constant
3) Viscosity of Medium
4) Average Shear Rate
5) Temperature
6) Density of Particle
7) Density of Medium
8) Dielectric Permittivity
9) Ionic Concentration
10) Valence of ionic Species
11) Electronic Charge
12) Surface Charge
13) Hamaker Constant

Input Parameters:
1, 13

Hamaker Theory

van der Waals Attractive Energy

Input Parameters:
1, 2, 5, 8, 9, 10, 11, 12, 13

Gouy-Chapman Theory

Electrostatic Repulsive Interaction Energy

Input Parameters:
1, 2, 5

Total Interaction Energy

Stability Ratio

Map of Aggregation Coefficient

Initial Particle Size Distribution

Population Balance Framework

Particle Size Distribution

Input Parameters:
1, 2, 3, 4

Perikinetic Collision Mechanism

Orthokinetic Collision Mechanism

Transport Limited Rate Constant

Differential Sedimentation Collision Mechanism

Map of Aggregation Coefficient

Figure 3.28. Flow Diagram of Mathematical Model
3.8 Summary

This chapter has presented a general mathematical model for colloidal aggregation. A population balance framework is the basis of this model. The Smoluchowski kinetics are used with the perikinet ic and orthokinetic collision mechanisms. These rates are modified to include colloidal stability using stability ratios. The sum of the van der Waals and electrostatic interaction energy are used to evaluate the stability ratios. Van der Waals interaction energy is computed using the Hamaker theory, and the electrostatic interaction is computed using the linear and non-linear Poisson-Boltzmann equation for flat plates coupled with the integration method of Papadopoulos and Cheh (1984). Discretization and solution of the population balance equations is solved using the Litster et al (1995), and the Wynn (1996) methods. Models of the discretization error were presented which shows the discretization method to provide adequate levels of accuracy.

The general nature of this model makes it suitable for both industrial and academic applications. The following chapters present the mathematical model experiments, and a comparison of experiments with mathematical model.
CHAPTER 4: EXPERIMENTS CONDUCTED BY MATHEMATICAL MODEL

4.1 Introduction
This chapter will show the experimental results from the mathematical model. Discretizing parameters, surface charge, fractal dimension, temperature, viscosity, ionic concentration, shear rate, diameter sizes and simultaneous perikinetic and orthokinetic collision mechanisms are studied to learn the capabilities of the model and to ensure agreement with current literature on colloidal aggregation.

4.2 The Effect of Discretizing Parameters on the Model
As the discretizing parameter q increases, there is also an increase in the total number of bins to cover a given particle size range. For example, to cover a size range between 0.01 to 10 microns, the following total number of bins, Z, are needed, as shown in Table 4.1.

Table 4.1 Discretizing Parameter versus Total Number of Bins

<table>
<thead>
<tr>
<th>Discretizing Parameter, Q</th>
<th>Total Number of Bins, Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
</tr>
<tr>
<td>3</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td>120</td>
</tr>
<tr>
<td>5</td>
<td>150</td>
</tr>
<tr>
<td>6</td>
<td>180</td>
</tr>
</tbody>
</table>
Increasing \( q \) increases the accuracy of the model because there are more bins to represent the actual particle concentration. Refer to Section 3.5.5 to review the reduction in error with increasing \( q \).

figure

Figure 4.1. Comparison of Discretizing Parameters for Perikineti Collision Mechanism
Figure 4.2. Comparison of Discretizing Parameters for Orthokinetic Mechanism

4.3 The Effect of Temperature and Viscosity on the Model

As the temperature of the suspension increases, aggregation becomes more rapid. Higher temperatures accelerate particle formation and growth.

\[ J_{Br} = \frac{4k_bT}{3^\frac{1}{2}} N_0^2 \]  

(4.1)

The above equation shows that increasing the temperature causes the perikinetic collision frequency to increase whereas increasing the viscosity of the medium reduces the collision frequency.
Figure 4.3. Temperature Comparison

In the case of orthokinetic aggregation, the temperature increase also increases natural particle Brownian motion, and enhances the efficiency of the mixing (especially in higher viscosities).
Figure 4.4. Viscosity Comparison

The model shows that aggregation slows rapidly with increasing viscosity. The increasing viscosity of the medium prevents the particles from undergoing natural Brownian motion. In the case of the orthokinetic collision mechanism, when the viscosity increases, it becomes harder to mix the solution, which impedes aggregation.

4.4 The Effect of Diameter Size on the Model

In perikinetiic and orthokinetic aggregation, aggregates rapidly form when larger and smaller size particles are in a suspension together. As shown in Figure 4.5 and 4.6, the diameter range of \(0.01 \times 10^{-6}\) to \(5.0 \times 10^{-6}\) and \(0.1 \times 10^{-6}\) to \(10.0 \times 10^{-6}\) had the most rapid aggregation due to the large variation of particle sizes in this group. The smaller particle size group (\(0.01 \times 10^{-6}\) to \(0.10 \times 10^{-6}\)) did not aggregate much under the perikinetiic or orthokinetic collision mechanism.
Figure 4.5. Diameter Size Comparison for Perikinetic Aggregation

Figure 4.6. Diameter Size Comparison for Orthokinetic Aggregation
4.5 The Effect of Salt Concentration on the Model

The addition of a salt to a suspension produces charged ions that reduce the effective distance of the electrostatic interactions. This occurs by increasing the solution ionic strength and suppressing the thickness of the layer of ions surrounding the particles. Around an ionic concentration of 0.1 M, the thickness of the double layer is reduced to the extent that particles can approach close enough for the attractive van der Waals forces to dominate (Spicer, 1997). The suspension is destabilized at this point, and the particles will aggregate if brought together by thermal motion or fluid shear. Particles can also be destabilized with charged polymers that adsorb to the particle surface and create a bridge between particles to form flocs. In either case, the result is a decreased electrostatic repulsion between particles. The destabilizing agent allows the particles to come close enough together to adhere. In most practical cases, the reduction in collision efficiency resulting from electrostatic effects is negligible if sufficient flocculant has been added (Spicer, 1997). As a function of ionic strength, the overall interaction undergoes a sharp transition from repulsive to attractive as shown in Figure 4.7 (McDuff and Heath, 2001). Figure 4.8 shows the behavior of the clay mineral kaolinite particles that were monitored at different ionic strengths (A = ionic strength of 0.036; B = ionic strength of 0.087, and C = ionic strength of 0.343 Clay Mineral Kaolinite) (McDuff and Heath, 2001).
Figure 4.7. Effect of Ionic Strength on Interaction Energy for Clay Mineral Kaolinite
As shown in Figure 4.9, the ionic concentration was adjusted from $1.0 \times 10^{-2}$ to 1000 mol/m$^3$, but only a small effect in aggregation rate is seen. This may be due to an already high degree of aggregation at the ionic concentration of $1.0 \times 10^{-2}$ mol/m$^3$. If the aggregation rate is reduced by adjusting other parameters (such as temperature), the salt concentration may have a larger influence on the particle aggregation according to this model.
4.6 The Effect of Hamaker Constants on the Model

As Hamaker constants become larger, the interaction energy becomes smaller as shown in Figure 4.10 (Fisher, 1998). Figure 4.11 shows a particle size increase with increasing Hamaker constant values.
Figure 4.10. Potential Energy of Interaction for Various Values of Hamaker Constant
Figure 4.11. Hamaker Constant Comparison

4.7 The Effect of Fractal Dimension and Primary Particle Sizes on the Model

If one considers the primary particle as a point object, then the fractal dimension of the growing aggregate should increase from a zero-dimensional point to a one-dimensional linear structure, to a branched chain of dimension on the order of two as the growth proceeds. The increase in dimension with growth is a natural consequence of the persistence of velocity for nano-particle Brownian motion combined with the random path of the colloiding particles. As growth proceeds, the presence of branches and the convoluted shape of the growing aggregate, reminiscent of the Brownian path of the colliding particles, shields the interior bonding sites from further growth. For this reason, three-dimensional growth is not possible, except by internal arrangement. The overall density of the aggregate, \( \frac{N}{R^3} \sim N^{(1-3/d_f)} \) diminishes with time in the asymptotic range since \( N \) is a monotonically increasing function of time (Bushell, 1998).
Figures 4.12 and 4.13 show the effect of primary particle size for the aggregation model. As the primary particle size increases, the aggregate growth decreases. The smaller primary particles have a high rate of Brownian motion, and are more likely to aggregate to larger colloidal molecules.

Figures 4.14 and 4.15 show an increasing rate of aggregation with smaller fractal dimension. The smaller fractal dimensions have more irregular structures with more void space, which enable these particles to attract oppositely charged molecules more readily. As the fractal dimension approaches a fractal dimension of 3.0, the particle aggregate becomes more compact and spherical in nature, which is harder to attract other particles. There are no dendritic arms to attract and catch particles.

Figure 4.12. Comparison of Primary Particle Size for Perikinetic Collision Mechanism
Figure 4.13. Comparison of Primary Particle Size for Orthokinetic Collision

Figure 4.14. Fractal Dimension Comparison for Perikinetic Collision
Figure 4.15. Fractal Dimension Comparison for Orthokinetic Collision Mechanism

4.8 The Effect of Surface Potential on the Model
The electric potential of the plane is equal to the work against electrostatic forces required to bring a unit electrical charge from infinity (from the bulk of solution) to that plane. If the plane is the surface of the particle, the potential is called surface potential, which measures the total potential of the double layer. If the surface potential is kept constant, the surface charge density must approach zero, as shown in Figure 4.16 (Pelton, 2003). This indicates that the surface is loosing charged groups. Figure 4.17 (Pelton, 2003) shows that with scalable potential, the initial slopes remain constant, and the corresponding potential drops. This gives lower interaction energy for the model, which gives a lower osmotic pressure between particle surfaces.
Figure 4.16. Constant Surface Potential Between Two Plates

Figure 4.17. Scaling Surface Potential Between Two Plates
Figure 4.18 shows the average scaling surface potential used in the model experimental runs.

![Surface Potential Versus Diameter](image)

Figure 4.18. Surface Potential Versus Diameter

4.9 The Effect of Shear Rate on the Model

As the shear rate increases, particle aggregation also increases until the shear rate gets high enough that there is simultaneous aggregation and deaggregation. Figure 4.19 shows that the aggregation rate increases with increasing shear rate, but after the shear rate is higher than forty, it is obvious that there is also deaggregation occurring because the particle diameter is slowly starting to decrease again sometime during the 20 – 50 hour time period. Based upon the graph, it seems that the higher the shear rate, the faster deaggregation will begin.
4.10 The Effect of Simultaneous Perikinetic and Orthokinetic Collision Mechanisms
Swift and Friedlander (1964) analyzed the kinetics of simultaneous orthokinetic and perikinetic coagulation by assuming the two mechanisms were additive. They found good agreement of a monodisperse model with experimental data for the aggregation of polystyrene particles.

To compare the collision frequencies due to shear flow that with due to Brownian motion, their ratio is characterized by the Peclet number which is obtained by dividing equation 2.13 by 2.7 (Agarwal, 2002).

\[
P_e = \frac{4[JGa^3]}{k_BT}
\]  
(4.2)
where $\nu$ is the fluid viscosity, $k$ is Boltzmann’s constant and $T$ is absolute temperature. According to Agarwal (2002), if $\text{Pe} >> 1$, shear flow dominates, but if $\text{Pe} << 1$, Brownian motion will dominate.

![Peclet Number versus Particle Diameter](image)

Figure 4.20. Peclet Number Versus Particle Diameter

Some experiments were conducted with the mathematical model with the perikinetict and orthokinetic collision mechanism. The parameters for these experiments are listed Table 4.2.
Table 4.2. Experimental Parameters for Perikineti c and Orthokinetic Experiments

<table>
<thead>
<tr>
<th>Experimental Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smallest Particle Diameter (m)</td>
<td>0.01E-6</td>
</tr>
<tr>
<td>Largest Particle Diameter (m)</td>
<td>5.0E-6</td>
</tr>
<tr>
<td>Number of Equations Covering particle range</td>
<td>81</td>
</tr>
<tr>
<td>Experimental Initial Condition (parts per mL)</td>
<td>8.399e+10</td>
</tr>
<tr>
<td>Mean of Initial Distribution</td>
<td>0.102E-06</td>
</tr>
<tr>
<td>Standard Deviation of Initial Distribution</td>
<td>0.0076E-6</td>
</tr>
<tr>
<td>Viscosity</td>
<td>1.001 cP</td>
</tr>
<tr>
<td>Temperature</td>
<td>293.15 K</td>
</tr>
<tr>
<td>G</td>
<td>varies</td>
</tr>
<tr>
<td>Fractal Dimension</td>
<td>1.7</td>
</tr>
</tbody>
</table>

The first set of experiments involve using the perikinetic collision mechanism and stability ratio for Peclet numbers less than 1, and using the orthokinetic collision mechanism and its stability ratio for Peclet numbers greater than 1. Figures 4.21 through 4.25 show the results of these experiments with different shear rates to change the Peclet numbers.
Figure 4.21. Log of Aggregation Coefficient, $G = 1$, Peclet < 1

Figure 4.22. Log of Stability Ratios, $G = 1$, Peclet < 1
Figure 4.23. Log of Stability Ratios, G = 70, Peclet < 1

Figure 4.24. Log of Stability Ratios, G = 70, Peclet < 1
Zeichner and Schowalter (1979) found that for a ratio of shear- to Brownian-induced collision frequencies < 5 and $G < 400 \text{ s}^{-1}$, Brownian aggregation affected (enhanced) shear-induced aggregation. They did, however, note that shear controlled the aggregation rate for all shear rates (100-1800 $\text{ s}^{-1}$) and concluded that Brownian collisions were important only for particles brought close together by shearing. Feke and Schowalter (1983) considered shear-dominated aggregation when small amounts of Brownian coagulation are present and concluded that Equation 4.2 could under-predict the shear-induced coagulation rate for values of the Peclet number, $\text{Pe} < 290$ and over-predict it for $\text{Pe} > 290$.

The next set of experiments involve using the perikineti collision mechanism and stability ratio for Peclet numbers less than 290, and using the orthokinetic collision mechanism and its stability ratio for Peclet numbers greater than 290. Figures 4.26 through 4.30 show the results of these experiments with different shear rates to change the Peclet numbers.
Figure 4.26. Log of Aggregation Coefficient for $G = 10$ and the Peclet number $<290$

Figure 4.27. Log of Stability Ratios for $G = 10$ and the Peclet number $<290$
Figure 4.28. Log of Aggregation Coefficient for G=20

Figure 4.29. Log of Stability Ratios for G=20

118
Figure 4.30. Perikinetic and Orthokinetic Aggregation

Han and Lawler (1992) assumed additivity of different aggregation collision mechanisms and calculated that Brownian motion was relevant during aggregation only when at least one of the colliding particles is less than 1 μm in diameter. Kusters et al. (1996) found that polydisperse coagulation models assuming additivity most accurately matched experimental data for turbulent coagulation.

The final set of experiments involve the addition of the perikinetic aggregation coefficients with the orthokinetic aggregation coefficients. Figures 4.31 through 4.34 show the results of these experiments with different shear rates.
Figure 4.31. Log of Perikinetic and Orthokinetic Collision Mechanism where G = 20

Figure 4.32. Log of Stability Ratios for G = 20
Figure 4.33. Log of Aggregation Coefficients for $G = 20$

Figure 4.34. Addition of Perikinetic and Orthokinetic Aggregation

121
4.11 Summary
This chapter showed the experimental results from the mathematical model. Discretizing parameters, surface charge, fractal dimension, temperature, viscosity, ionic concentration, shear rate, diameter sizes and simultaneous perkinetic and orthokinetic collision mechanisms were varied to learn the capabilities of the model. There was good agreement with current literature on colloidal aggregation.
CHAPTER 5: COMPARISON OF MATHEMATICAL MODEL WITH EXPERIMENTS

5.1 Introduction
This chapter discusses the experiments that were performed by Scott Fisher (1998) to validate the mathematical model. A description of the materials, experimental procedure, and the setup used in the aggregation experiments will be described. Experiments were conducted for the perikinetic and orthokinetic transport mechanisms. Particle sizes were measured using a particle analyzer, electron microscopy and UV/Visible spectroscopy to provide particle size analysis throughout the course of the aggregation process.

5.2 Materials
The general class of colloids was represented by polystyrene latex because its physical properties, (2) density, (3) refractive index, and (4) surface charge are all well known. Polystyrene was also chosen because it has a density close to that of salt solutions used for suspension, which limits the effects of sedimentation. Monodispersed polystyrene standards from Duke Scientific Corporation were used, and the particle properties are displayed in Table 5.1.
Table 5.1. Properties of Particle Standards

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Nominal Diameter [nm]</th>
<th>Mean Diameter [nm]</th>
<th>Standard Deviation [nm]</th>
<th>Density (g/mL)</th>
<th>Index of Refraction at 589 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS1</td>
<td>100</td>
<td>102</td>
<td>7.6</td>
<td>1.05</td>
<td>1.59</td>
</tr>
<tr>
<td>PS2</td>
<td>150</td>
<td>155</td>
<td>3.1</td>
<td>1.05</td>
<td>1.59</td>
</tr>
<tr>
<td>PS3</td>
<td>500</td>
<td>503</td>
<td>6.3</td>
<td>1.05</td>
<td>1.59</td>
</tr>
</tbody>
</table>

These concentrated dispersions were diluted by three orders of magnitude so that UV/Vis spectroscopy could be used for particle size analysis. The same stock solution is used for all experimental runs to aid in reproducibility. Table 4.2 shows the volumes used to create the stock solutions, and relevant solution properties.

Table 5.2 Properties of Particle Stock Solutions

<table>
<thead>
<tr>
<th>Particle Standard</th>
<th>Volume of Standard (mL)</th>
<th>Volume of Solution (mL)</th>
<th>Mass Concentration (g/mL)</th>
<th>Particle Concentration (part/mL)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS1</td>
<td>0.75</td>
<td>50</td>
<td>$1.5 \times 10^{-4}$</td>
<td>$2.57 \times 10^{11}$</td>
<td>5.70</td>
</tr>
<tr>
<td>PS2</td>
<td>0.3</td>
<td>50</td>
<td>$7.2 \times 10^{-5}$</td>
<td>$3.52 \times 10^{10}$</td>
<td>5.93</td>
</tr>
<tr>
<td>PS3</td>
<td>1.7</td>
<td>100</td>
<td>$1.7 \times 10^{-4}$</td>
<td>$2.43 \times 10^{9}$</td>
<td>6.17</td>
</tr>
</tbody>
</table>
5.3 Particle Size Distributions
The particle sizes for the three-particle standard used in experiments were measured using three particle size units: electron microscopy, a Microtrac® UPA 150 Ultrafine Particle Analyzer, and a Hewlett Packard 8453 UV/Visible Spectrophotometer (Fisher, 1998). Table 5.3 shows a comparison of the mean and standard deviation for each of the three particle standards.

Table 5.3 Summary of the Initial Particle Size Distribution for Standards

<table>
<thead>
<tr>
<th>Particle Standard</th>
<th>Microscopy Mean (nm)</th>
<th>Microtrac UPA 150 Mean (nm)</th>
<th>Microtrac UPA 150 Standard Deviation (nm)</th>
<th>UV/Vis Spectroscopy Mean (nm)</th>
<th>UV/Vis Spectroscopy Standard Deviation (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS1</td>
<td>102</td>
<td>91</td>
<td>18.8</td>
<td>104</td>
<td>0.3</td>
</tr>
<tr>
<td>PS2</td>
<td>155</td>
<td>142</td>
<td>26.3</td>
<td>156</td>
<td>0.2</td>
</tr>
<tr>
<td>PS3</td>
<td>503</td>
<td>471</td>
<td>80.0</td>
<td>529</td>
<td>0.4</td>
</tr>
</tbody>
</table>

5.4 Measurement of Surface Potentials
Surface charge is important in modeling aggregation phenomena because it dominates particle dispersion and aggregation. Surface potential measurements were taken using a Zeta Plus Zeta Potential Analyzer manufactured by Brookhaven Instruments Limited. Zeta potential measurements were conducted for three concentrations of potassium chloride: 0.1 M, 1 x 10^{-3} M, and 1 x 10^{-4} M (Fisher, 1998). The samples were prepared by mixing 100 mL of the appropriate potassium chloride solution, adding 0.5 ml of concentrated particle
standard, and then adjusting the pH with the addition of either concentrated acid, HCl or base NaOH (Fisher, 1998).

![Zeta Potential for Polystyrene](image.png)

Figure 5.1. Zeta Potential for Polystyrene

The salt concentration presented in Figure 5.1 agrees with the Gouy-Chapman theory in the fact when the salt concentration is increased, the electric double layer is compressed, yielding lower effective surface charge (Fisher, 1998). The zeta potential also follows the theory because when the pH is decreased, the ionizable groups on the surface of the polystyrene particles become protonated, which reduces the surface charge.

5.5 Measurement of Aggregation Phenomenon
The experiments were conducted at various pH and salt concentrations, and allowed to aggregate by perikinetic or orthokinetic aggregation. Particle aggregation was then characterized by average particle size as a function of experimental time.
The experimental data was calculated from the turbidity measurements (Fisher, 1998). Refer to Fisher (1998) for the algorithms used to produce average particle size, and the two population average particle size calculation.

The mathematical model will use the same parameters and initial conditions as were used and measured in the experiments. The fractal dimension used for this comparison will either be 1.7 for diffusion-limited experiments or 2.3 for reaction-limited or mixed systems. These values are the most commonly reported values from other experimental techniques (Fisher, 1998).

5.6 Experimental Runs

The experiments that were conducted were performed to test the validity of the perikinetiс and orthokinetic collision mechanisms. Experiments A and B are used to determine the validity of the perikinetiс collision mechanism for polystyrene particles of various sizes. Experiments C, D, E, and F will be used to test the applicability of the orthokinetic mechanism. To ensure that the experiment conducted was in the transport-limited aggregation regime, the solution conditions, pH, and KCl concentration were chosen to minimize the surface potential. (Fisher, 1998). Particle sizes between 100 nm and 503 nm were used as the particle size initial conditions.

For comparison, the following notation will be used for the Figures: EXP Davg is the experimental number average particle diameter, EXP D1 is the experimental number average particle diameter for the smaller of the two population analysis, and EXP D2 is the experimental number average particle diameter for the larger of the two population analysis. MODEL Davg, MODEL D1, and MODEL D2 are the results of the mathematical model presented in this paper. SF MODEL Davg, SF MODEL D1, ans SF MODEL D2 are the results of Fisher’s mathematical model (1998) which excluded attraction and repulsion forces and stability ratios.
5.7 Comparison

5.7.1 Experiment A

Table 5.4. Experimental Parameters for Experiment A

<table>
<thead>
<tr>
<th>Experimental Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Collision Mechanism</td>
<td>Perikinetic</td>
</tr>
<tr>
<td>Smallest Particle Diameter (m)</td>
<td>0.06E-6</td>
</tr>
<tr>
<td>Largest Particle Diameter (m)</td>
<td>4.0E-6</td>
</tr>
<tr>
<td>Number of Equations Covering particle range</td>
<td>91</td>
</tr>
<tr>
<td>Experimental Initial Condition (parts per mL)</td>
<td>9.383995E+10</td>
</tr>
<tr>
<td>Mean of Initial Distribution</td>
<td>0.102E-06</td>
</tr>
<tr>
<td>Standard Deviation of Initial Distribution</td>
<td>0.0076E-6</td>
</tr>
<tr>
<td>Viscosity (cP)</td>
<td>1.001 cP</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>293.15 K</td>
</tr>
<tr>
<td>Fractal Dimension</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Table 5.5. Degree of Aggregation for Experiment A

<table>
<thead>
<tr>
<th>Iagg</th>
<th>Scott Fisher Model</th>
<th>0</th>
<th>0.35149</th>
<th>0.52134</th>
<th>0.62122</th>
<th>0.6869</th>
<th>0.73334</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.76788</td>
<td>0.8158</td>
<td>0.94912</td>
<td>0.9597</td>
<td>0.96788</td>
<td>0.76788</td>
</tr>
<tr>
<td>Iagg</td>
<td>Model</td>
<td>0</td>
<td>0.18309</td>
<td>0.31182</td>
<td>0.40704</td>
<td>0.48019</td>
<td>0.53807</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.58494</td>
<td>0.65609</td>
<td>0.8987</td>
<td>0.92073</td>
<td>0.93785</td>
<td>0.58494</td>
</tr>
</tbody>
</table>
Figure 5.2. Log of Perikineti Collision Mechanism for Experiment A

Figure 5.3. Log of Stability Ratios for Experiment A
Figure 5.4. Log of Aggregation Coefficient for Experiment A

Figure 5.5. Particle Concentration versus Time for Experiment A
Figure 5.6. Particle Concentration versus Particle Diameter for Experiment A
Figure 5.7. Actual versus Mathematical Model Experiments (Experiment A)
5.7.2 Experiment B

Table 5.6. Experimental Parameters for Experiment B

<table>
<thead>
<tr>
<th>Experimental Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Collision Mechanism</td>
<td>Perikinetic</td>
</tr>
<tr>
<td>Smallest Particle Diameter (m)</td>
<td>0.3E-6</td>
</tr>
<tr>
<td>Largest Particle Diameter (m)</td>
<td>2.0E-6</td>
</tr>
<tr>
<td>Number of Equations Covering particle range</td>
<td>50</td>
</tr>
<tr>
<td>Experimental Initial Condition (parts per mL)</td>
<td>1.475E+10</td>
</tr>
<tr>
<td>Mean of Initial Distribution</td>
<td>0.503E-06</td>
</tr>
<tr>
<td>Standard Deviation of Initial Distribution</td>
<td>0.0063E-6</td>
</tr>
<tr>
<td>Viscosity (cP)</td>
<td>1.001 cP</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>293.15 K</td>
</tr>
<tr>
<td>Fractal Dimension</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Table 5.7. Degree of Aggregation for Experiment B

<table>
<thead>
<tr>
<th>$I_{agg}$ Scott Fisher Model</th>
<th>0</th>
<th>0.06443</th>
<th>0.12116</th>
<th>0.21642</th>
<th>0.29325</th>
<th>0.75164</th>
<th>0.78586</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{agg}$ Model</td>
<td>0</td>
<td>0.02078</td>
<td>0.04081</td>
<td>0.07874</td>
<td>0.11407</td>
<td>0.14706</td>
<td>0.17791</td>
</tr>
</tbody>
</table>
Figure 5.8. Log of Perikinetiic Collision Mechanism for Experiment B

Figure 5.9. Log of Stability Ratios for Experiment B
Figure 5.10. Log of Aggregation Coefficients for Experiment B

Figure 5.11. Particle Concentration versus Time for Experiment B
Figure 5.12. Particle Concentration versus Particle Diameter for Experiment B
Figure 5.13. Actual versus Mathematical Model Experiments (Experiment B)
5.7.3 Experiment C

Table 5.8. Experimental Parameters for Experiment C

<table>
<thead>
<tr>
<th>Experimental Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Collision Mechanism</td>
<td>Orthokinetic</td>
</tr>
<tr>
<td>Smallest Particle Diameter (m)</td>
<td>0.06E-6</td>
</tr>
<tr>
<td>Largest Particle Diameter (m)</td>
<td>3.0E-6</td>
</tr>
<tr>
<td>Number of Equations Covering particle range</td>
<td>51</td>
</tr>
<tr>
<td>Experimental Initial Condition (parts per mL)</td>
<td>8.399E+10</td>
</tr>
<tr>
<td>Mean of Initial Distribution</td>
<td>0.102E-06</td>
</tr>
<tr>
<td>Standard Deviation of Initial Distribution</td>
<td>0.0076E-6</td>
</tr>
<tr>
<td>Viscosity (cP)</td>
<td>1.001 cP</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>293.15</td>
</tr>
<tr>
<td>Fractal Dimension</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Table 5.9. Degree of Aggregation for Experiment C

<table>
<thead>
<tr>
<th>$L_{agg}$ Scott Fisher Model</th>
<th>0</th>
<th>0.38914</th>
<th>0.61285</th>
<th>0.74516</th>
<th>0.82591</th>
<th>0.87681</th>
<th>0.90997</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.93227</td>
<td>0.94774</td>
<td>0.95874</td>
<td>0.96668</td>
<td>0.97246</td>
<td>0.97671</td>
<td>0.97989</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>$L_{agg}$ Model</th>
<th>0</th>
<th>0.4131</th>
<th>0.6269</th>
<th>0.74556</th>
<th>0.81675</th>
<th>0.86248</th>
<th>0.89357</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>0.91566</td>
<td>0.93194</td>
<td>0.94426</td>
<td>0.9538</td>
<td>0.96132</td>
<td>0.96734</td>
<td>0.9722</td>
</tr>
</tbody>
</table>
Figure 5.14. Log of Orthokinetic Collision Mechanism for Experiment C

Figure 5.15. Log of Aggregation Coefficient for Experiment C
Figure 5.16. Particle Concentration versus Time for Experiment C

Figure 5.17. Particle Concentration versus Particle Diameter for Experiment C
Figure 5.18. Log of Stability Ratios for Experiment C
Figure 5.19. Actual versus Mathematical Model Experiments (Experiment C)
5.7.4 Experiment D

Table 5.10. Experimental Parameters for Experiment D

<table>
<thead>
<tr>
<th>Experimental Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Collision Mechanism</td>
<td>Orthokinetic</td>
</tr>
<tr>
<td>Smallest Particle Diameter (m)</td>
<td>0.06E-6</td>
</tr>
<tr>
<td>Largest Particle Diameter (m)</td>
<td>4.0E-6</td>
</tr>
<tr>
<td>Number of Equations Covering particle range</td>
<td>55</td>
</tr>
<tr>
<td>Experimental Initial Condition (parts per mL)</td>
<td>6.122E+10</td>
</tr>
<tr>
<td>Mean of Initial Distribution</td>
<td>0.102E-06</td>
</tr>
<tr>
<td>Standard Deviation of Initial Distribution</td>
<td>0.0076E-6;</td>
</tr>
<tr>
<td>Viscosity (cP)</td>
<td>1.001</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>293.15</td>
</tr>
<tr>
<td>Fractal Dimension</td>
<td>1.5</td>
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</table>

Table 5.11. Degree of Aggregation for Experiment D

<table>
<thead>
<tr>
<th>( I_{agg} )</th>
<th>0</th>
<th>0.9036</th>
<th>0.97639</th>
<th>0.9891</th>
<th>0.99261</th>
<th>0.99428</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scott</td>
<td>0.99529</td>
<td>0.99597</td>
<td>0.99647</td>
<td>0.99685</td>
<td>0.99715</td>
<td>0.9974</td>
</tr>
<tr>
<td>Fisher Model</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Model</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( I_{agg} )</td>
<td>0</td>
<td>0.87414</td>
<td>0.95446</td>
<td>0.9779</td>
<td>0.98715</td>
<td>0.99127</td>
</tr>
<tr>
<td></td>
<td>0.99318</td>
<td>0.99424</td>
<td>0.99493</td>
<td>0.99544</td>
<td>0.99583</td>
<td>0.99614</td>
</tr>
</tbody>
</table>
Figure 5.20. Stability Ratios for Experiment D

Figure 5.21. Log of Orthokinetic Collision Mechanism for Experiment D
Figure 5.22. Log of Aggregation Coefficients for Experiment D

Figure 5.23. Particle Concentration versus Time for Experiment D
Figure 5.24. Particle Concentration versus Particle Diameter for Experiment D
Figure 5.25. Actual versus Mathematical Model Experiments (Experiment D)
5.7.5 Experiment E

Table 5.12. Experimental Parameters for Experiment E

<table>
<thead>
<tr>
<th>Experimental Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Collision Mechanism</td>
<td>Orthokinetic</td>
</tr>
<tr>
<td>Smallest Particle Diameter (m)</td>
<td>0.08E-6</td>
</tr>
<tr>
<td>Largest Particle Diameter (m)</td>
<td>2.0E-6</td>
</tr>
<tr>
<td>Number of Equations Covering particle range</td>
<td>42</td>
</tr>
<tr>
<td>Experimental Initial Condition (parts per mL)</td>
<td>3.5461e+9</td>
</tr>
<tr>
<td>Mean of Initial Distribution</td>
<td>0.155E-06</td>
</tr>
<tr>
<td>Standard Deviation of Initial Distribution</td>
<td>0.0031E-6</td>
</tr>
<tr>
<td>Viscosity (cP)</td>
<td>1.001 cP</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>293.15 K</td>
</tr>
<tr>
<td>Fractal Dimension</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Table 5.13. Degree of Aggregation for Experiment E

<table>
<thead>
<tr>
<th>$L_{agg}$ Scott Fisher Model</th>
<th>$L_{agg}$ Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.3458</td>
</tr>
<tr>
<td>0.3597</td>
<td>0.5619</td>
</tr>
<tr>
<td>0.3597</td>
<td>0.5670</td>
</tr>
<tr>
<td>0.6993</td>
<td>0.6910</td>
</tr>
<tr>
<td>0.7883</td>
<td>0.7690</td>
</tr>
<tr>
<td>0.8472</td>
<td>0.8209</td>
</tr>
<tr>
<td>0.8869</td>
<td>0.8571</td>
</tr>
<tr>
<td>0.9143</td>
<td>0.8834</td>
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</tbody>
</table>
Figure 5.26. Actual versus Mathematical Model Experiments (Experiment E)
5.7.6 Experiment F

Table 5.14. Experimental Parameters for Experiment F

<table>
<thead>
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<th>Value</th>
</tr>
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<tbody>
<tr>
<td>q</td>
<td>1</td>
</tr>
<tr>
<td>Smallest Particle Diameter (m)</td>
<td>0.2E-6</td>
</tr>
<tr>
<td>Largest Particle Diameter (m)</td>
<td>3.0E-6</td>
</tr>
<tr>
<td>Number of Equations Covering particle range</td>
<td>12</td>
</tr>
<tr>
<td>Experimental Initial Condition (parts per mL)</td>
<td>1.5e+8</td>
</tr>
<tr>
<td>Mean of Initial Distribution</td>
<td>0.503E-06</td>
</tr>
<tr>
<td>Standard Deviation of Initial Distribution</td>
<td>0.0063E-6</td>
</tr>
<tr>
<td>Viscosity (cP)</td>
<td>1.001 cP</td>
</tr>
<tr>
<td>G</td>
<td>30</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>293.15 K</td>
</tr>
<tr>
<td>Fractal Dimension</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Table 5.15. Degree of Aggregation for Experiment F

<table>
<thead>
<tr>
<th>I_{agg} Scott Fisher Model</th>
<th>0</th>
<th>0.10811</th>
<th>0.20322</th>
<th>0.36075</th>
<th>0.48338</th>
<th>0.57934</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.65486</td>
<td>0.71466</td>
<td>0.80035</td>
<td>0.8556</td>
<td>0.89165</td>
<td>0.91556</td>
</tr>
<tr>
<td>I_{agg} Model</td>
<td>0</td>
<td>0.11556</td>
<td>0.21544</td>
<td>0.37573</td>
<td>0.49508</td>
<td>0.58471</td>
</tr>
<tr>
<td></td>
<td>0.65282</td>
<td>0.70531</td>
<td>0.77901</td>
<td>0.82675</td>
<td>0.85932</td>
<td>0.88254</td>
</tr>
</tbody>
</table>
Figure 5.27. Actual versus Mathematical Model Experiments (Experiment F)

5.8 Conclusion
From transport-limited experiments presented in this chapter, it is evident that the mathematical model does an excellent job of predicting the average and two population average particle sizes. The perikinetic experiments show some deviations at long times, while at shorter times, the model predictions are in agreement with the experimental results. The orthokinetic collision mechanism shows agreement with experimental results. The general trends in both particle size and stirring rate support the correctness of the orthokinetic mechanism. From the experimental range used, it can be stated that the mathematical model hold true for stirring rates between 120 and 550 rpm, however, there might be evidence of the onset of breakup in the higher stirring range. Also initial particle sizes and final sizes stretch a range of 0.1 microns to 1.5 microns. This adequately covers the range of applicability for most colloidal systems.
CHAPTER 6: CONCLUSIONS

6.1 Mathematical Model
The mathematical model presented in this work provides a description of aggregation in a batch unit. The model integrates several different mechanisms and ideas that are presented in literature. This model is flexible because it can include the addition of many parameters that pertain to aggregation of a specific system. The population balance is necessary for a full description of the aggregation process. The inclusion of the van der Waals attractive and electrostatic repulsive forces and the stability ratios provided a more accurate description and model for colloidal particle aggregation. The mathematical model can easily be adjusted and updated to investigate modifications to the collision mechanisms, stability ratios, interaction energy forces etc.

6.2 Experiments Conducted with Mathematical Model
A number of experiments were conducted with the mathematical model. Discretizing parameters, surface charge, fractal dimension, temperature, viscosity, ionic concentration, shear rate, diameter sizes and simultaneous perikinetic and orthokinetic collision mechanisms were varied to learn the capabilities of the model. There was good agreement with current literature on colloidal aggregation.

6.3 Comparison of Mathematical Model with Experiments
The mathematical model agrees well with experimental results over a size range of 0.1 to 1.5 microns for both the orthokinetic and perikinetic models. The model provides level of accuracy higher than those of the particle size measurements when considering the average and the two population average size particle sizes. One hindrance in the comparison is the fractal nature of the fractal aggregates in that the true fractal dimension is not known.
6.4 Future Work

This mathematical model sheds some basic insight into the nature of colloidal aggregates, but there are many assumptions and techniques that may impose error into the mathematical model. Several factors should be addressed in the future:

1) The inclusion of additional forces such as Born repulsion and steric interaction,

2) Surface properties, such as surface roughness (especially for the smaller colloidal particles, where surface properties begin to dominate the particle’s properties),

3) Stability ratios need to be determined for differential sedimentation. The stability ratios for differential sedimentation are sometimes estimated in literature, but there is currently no definite mathematical relation to describe the “stickiness factor” for differential settling,

4) More accurate stability ratios need to be determined for orthokinetic sedimentation. The orthokinetic stability ratio used in this mathematical model has good agreement with the actual experiments conducted, but the stability ratio used is an estimate stability ratio from Potanin (1991),

5) Cluster-cluster aggregation, or collisions between multiple particles,

6) Better measurement for the input parameters to the model. An analysis of the propagation of error in the model should be conducted in order to identify the most important process parameters. For example, the calculation of average shear rate is a parameter with significant uncertainty because it depends upon the vessel used.
REFERENCES


Biggs C.A. Activated Sludge Flocculation: Investigating the Effect of Shear Rate and Cation Concentration on Flocculation Dynamics. PhD, University of Queensland, Australia, 2000.

Bushell, Graeme. “Primary Particle Polydispersity In Fractal Aggregates”. The University of New South Wales School of Chemical Engineering and Industrial Chemistry. PHD Dissertation, June 1998.


157


APPENDICES
Appendix 1: Criterion for Monotonic or Concave Potential

An electrostatic potential profile \( \phi \) is defined by the following differential equation:

\[
\frac{d\phi}{dx} = \pm \sqrt{2 \cosh(\phi) + C}
\]

and the boundary conditions:

\[
\phi(0) = \phi \quad \text{and} \quad \phi(Xd) = \phi
\]

where \( Xd \) is the distance of separation between plates. Notice that the square root in the RHS of equation A.1.2 forces the inequality:

\[
\sqrt{2 \cosh(\phi) + C} \geq 0
\]

If \( \phi \) is monotonic, the distance of separation between two plates can be expressed by integrating A.1.1 as:

\[
Xd = \int_0^\phi \frac{d\phi}{\sqrt{2 \cosh(\phi) + C}}
\]

Let \( Xd_a \) and \( Xd_b \) be the distances of separation corresponding to two monotonic electrostatic potential profiles between plates with boundary conditions A.1.2. Let \( Ca \) and \( Cb \) be the constants corresponding to \( Xd_a \) and \( Xd_b \). If \( Ca > Cb \),

\[
\int_0^{\phi} \frac{d\phi}{\sqrt{2 \cosh(\phi) + Ca}} > \int_0^{\phi} \frac{d\phi}{\sqrt{2 \cosh(\phi) + Cb}}
\]

hence \( Xd_a < Xd_b \) and as a constant \( C \) decreases the distance of separation between the plates \( Xd \) increases. A direct consequence of A.1.3 is that:

\[
C \geq -2 \cosh(\phi)
\]
Appendix 1: (Continued)

And therefore the minimum value of C, which corresponds to the maximum value of Xd is -2 \( \cosh(\bar{\lambda}) \). If \( x_{\text{ref}} \) is the maximum value of Xd,

\[
x_{\text{ref}} = \frac{\alpha}{2 \cosh(\bar{\lambda}) \sqrt{2 \cosh(\bar{\lambda})}}
\]

A.1.7

As a conclusion, Xd > \( x_{\text{ref}} \) the distribution of the electrostatic potential is not monotonic and therefore must be concave.

Moreover, some conclusions may be drawn about the range of values of C for the concave case. If \( \Box \) is concave, it reaches its minimum when:

\[
\frac{d\Box}{dx} = 0 = \sqrt{2 \cosh(\bar{\lambda}_{\text{min}})} + C
\]

A.1.8

or

\[
C = -2 \cosh(\bar{\lambda}_{\text{min}})
\]

A.1.9

In general, \( \cosh(\bar{\lambda}) \geq 1 \), hence from A.1.9 it follows that C \( \leq -2 \). It was seen above that \( \Box \) was monotonic if C > \( -2 \) \( \cosh(\bar{\lambda}) \) and therefore it must be concave otherwise. This sets the range \( [-2\cosh(\bar{\lambda}), -2] \) for C if \( \Box \) is concave.
Appendix 2: Behavior of Concave Electrostatic Potential as C Varies.

The distance of separation between two plates when the electrostatic potential between them is concave can be expressed as (from Appendix 1):

\[
Xd = \frac{\xi}{\xi_{\text{min}} \sqrt{2 \cosh(\xi) - 2 \cosh(\xi_{\text{min}})}} + \frac{\eta}{\eta_{\text{min}} \sqrt{2 \cosh(\eta) - 2 \cosh(\eta_{\text{min}})}}
\]  

A.2.1

where \( \xi_{\text{min}} \) is an integration constant which corresponds physically to the minimum of the electrostatic surface potentials on the plates. The objective of this appendix is to show that \( Xd \) increases as \( \xi_{\text{min}} \) decreases. This property of equation A.2.1 is important in order to improve the efficiency of the algorithm employed to solve the PBE and compute interaction potential energies between plates.

Establishing the sign of the derivative will begin the proof in the interval of interest:

\[
\frac{dXd}{d\xi_{\text{min}}}
\]  

A.2.2

In order to accomplish this task, equation A.2.1 should be differentiated by means of Leibnitz’ rule for differentiation under the integral. If

\[
I(\xi) = \int_{x_1(\xi)}^{x_2(\xi)} f(x, \xi) dx
\]  

A.2.3

then

\[
\frac{dI(\xi)}{d\xi} = f(x_2, \xi) \frac{dx_2}{d\xi} \int_{x_1(\xi)}^{x_2(\xi)} f(x_1, \xi) \frac{dx_1}{d\xi} + \int_{x_1(\xi)}^{x_2(\xi)} \frac{df(x, \xi)}{d\xi} dx
\]  

A.2.4

Furthermore, it is only necessary to carry out the proof for one of the two integrals in A.2.1 since the result will be identical for both. If A.2.4 is applied to one of the integrals in A.2.1
Appendix 2: (Continued)

the following result is obtained:

\[
\frac{dI_1}{d\Omega_{\text{min}}} = \frac{1}{2 \cosh(\Omega) - 2 \cosh(\Omega_{\text{min}})} \frac{d\Omega_{\text{min}}}{d\Omega_{\text{min}}} + \frac{\Omega}{2 \cosh(\Omega) - 2 \cosh(\Omega_{\text{min}})} \left[ \frac{3}{2} \sinh(\Omega_{\text{min}}) \right]^{3/2} \sinh(\Omega_{\text{min}}) d\Omega
\]

A.2.5

The first term of the RHS of A.2.5 is an indetermination. Therefore the derivative searched for cannot be determined analytically by means of this method. In order to circumvent this situation, one of the intervals in Equation A.2.1 can be rewritten as:

\[
I_1 = \int_{\Omega_{\text{min}}}^{\Omega} \frac{d\Omega}{\sqrt{2 \cosh(\Omega) - 2 \cosh(\Omega_{\text{min}})}} + \int_{\Omega_{\text{min}}}^{\Omega} \frac{d\Omega}{\sqrt{2 \cosh(\Omega) - 2 \cosh(\Omega_{\text{min}})}}
\]

A.2.6

Since equation A.2.6 converges as will be shown below, in the limit as \( A \to \Omega \) the second integral in equation A.2.6 will approach zero. Applying equation A.2.4 to equation A.2.6 result in the following:

\[
\frac{dI_1}{d\Omega_{\text{min}}} = \frac{1}{\sqrt{2 \cosh(A) - 2 \cosh(\Omega_{\text{min}})}} \frac{dA}{d\Omega_{\text{min}}} + \frac{\Omega}{2 \cosh(\Omega) - 2 \cosh(\Omega_{\text{min}})} \left[ \frac{3}{2} \sinh(\Omega_{\text{min}}) \right]^{3/2} \sinh(\Omega_{\text{min}}) d\Omega
\]

A.2.7

In order to determine the sign of A.2.7 the following theorem from elementary calculus will be used:

163
Appendix 2: (Continued)

If \( g(x) \geq f(x) \geq h(x) \), then

\[
M = \int_a^b f(x) \, dx \geq \int_a^b g(x) \, dx \geq \int_a^b h(x) \, dx
\]

A.2.8

Since the following relationship holds:

\[
\int_i^e \geq \int_i^f \geq \int_i^g \geq 0
\]

also holds:

\[
\frac{\sinh(\int_i^e)}{\sinh(\int_i^f)} \geq 1
\]

A.2.9

Therefore,

\[
\frac{dI}{d\int_i^e} = A \int_i^e \frac{\sinh(\int_i^e)}{\sqrt{2 \cosh(A) \int_i^e 2 \cosh(\int_i^e)}} \, d\int_i^e + z
\]

A.2.10

\[
z = A \int_i^e \frac{1}{\sqrt{2 \cosh(A) \int_i^e 2 \cosh(\int_i^e)}} \, dA
\]

A.2.11

The integral in A.2.10 can be integrated analytically by means of transformation \( u = \cosh(\int_i^e) \). Equation A.2.10 becomes:

\[
\frac{dI}{d\int_i^e} = A \int_i^e \frac{1}{\sqrt{2 \cosh(\int_i^e) \int_i^e 2 \cosh(\int_i^e)}} \, d\int_i^e + z
\]

A.2.12

Evaluation of A.2.12:

\[
\frac{dI}{d\int_i^e} = A \int_i^e \frac{1}{\sqrt{2 \cosh(\int_i^e) \int_i^e 2 \cosh(\int_i^e)}} \, d\int_i^e + z \]z
\]

A.2.13

Taking the limit of A.2.13 results in:

164
Appendix 2: (Continued)

\[
\frac{dI_1}{d[I_{\text{min}}]} < \frac{1}{[\sqrt{2\cosh(I_{\text{min}})}][2\cosh(I_{\text{min}})]} < 0 \quad \text{A.2.14}
\]

It is evident that the sign of \(I_1\) will maintain for \(I_2\) and therefore it was established that:

\[
\frac{dXd}{d[I_{\text{min}}]} < 0 \quad \text{A.2.15}
\]

and therefore it was proved that as \(I_{\text{min}}\) decreases \(Xd\) increases in the range set in A.2.9. It still must be proved that A.2.6 converges. To accomplish this the same procedure is used in A.2.8 will be applied. In fact, the following inequality follows from equation A.2.1:

\[
I_1 < \frac{1}{\sinh(I_{\text{min}})} \left[ \sqrt{2\cosh(I)} \right] \frac{\sinh(I)}{\sqrt{2\cosh(I) \cdot 2\cosh(I_{\text{min}})}} d[I] \quad \text{A.2.16}
\]

The same transformation shown above \([u=\cosh(I)]\) is used to integrate A.2.16 and renders:

\[
I_1 < \sqrt{2\cosh(I) \cdot 2\cosh(I_{\text{min}})} \quad \frac{\sinh(I)}{\sinh(I_{\text{min}})} \quad \text{A.2.17}
\]

which means that \(X_d\) converges and sets an upper limit for it that may be useful in numerical evaluations of the integrals involved.
Appendix 3: Derivation of K terms for Adjustable Discretization of Litster et al.

Type 1 Interactions:

This derivation was performed in Chapter 3.

Type 2 Interactions:

The only combination for all interactions give particles in the ith interval is shown both particles are from the I-qth interval. It then follows that:

$$ R_{p,q}^2 = \frac{1}{2} \nu_{p,q} N_i^2 $$ \hspace{1cm} A.3.1

The factor _ ensures that the interaction is not counted twice.

Type 3 Interactions:

Consider interactions between particles in the I-pth and the jth interval where some of the resulting particles fall into the ith interval and some are too large. A particle of size between a and a + da in the jth interval must aggregate with a particle in the size range $2^{(l-p)q} < v < 2^{(l+1)q}$ from the I-pth interval to give a particle in the ith interval. The rate of formation of particles in the ith interval by such situations is:

$$ dR_{i,p,j}^{[3]} = \nu_i \nu_j N_i^2 N_j \frac{2^{(l+1)/q}}{2^{(l+p)/q}} \frac{2^{(l+p)/q}}{(2^{l+1})^2} da $$ \hspace{1cm} A.3.2

Integrating to get the total rate of successful interactions between the I-pth and the jth intervals gives:

$$ R_{i,p,j}^{[3]} = \nu_i \nu_j N_i^2 N_j 2^{(l+1)/q} \frac{2^{l+1}}{2} \left[ 2^{(l+p)/q} \right] $$ \hspace{1cm} A.3.3
Appendix 3: (Continued)

which yields the following value for $K_3$:

$$K_3 = \frac{2^{k/q} \prod 1}{2^{1/q} \prod 1} \frac{2^{1/q} + 1}{2(2^{1/q} \prod 1)} 2^{(j\lceil n \rceil)/q}$$  \hspace{1cm} A.3.4

Type 4 Interactions:

Consider the interactions between particles in the $i$th and $j$th intervals where some remove particles from the $i$th interval. A particle of size between $a$ and $a + da$ in the $j$th interval must interact with a particle in the size range $2^{(1+1)q} - a < \nu < 2^{(1+1)q}$ to remove particles in the $i$th. The total rate of successful collisions of this type is:

$$dR_{i,j}^{[4]} = \frac{\prod_{i,j} N_i^i N_j^j da}{2^{(i+j)/q} (2^{1/q} \prod 1)^2}$$  \hspace{1cm} A.3.5

Integration over the $j$th interval gives:

$$dR_{i,j}^{[4]} = \prod_{i,j} N_i^i N_j^j \frac{2^{1/q} + 1}{2(2^{1/q} \prod 1)} 2^{(j\lceil n \rceil)/q}$$  \hspace{1cm} A.3.6

Type 5 Interactions:

All combinations are successful in removing particles from the $i$th interval, and therefore:

$$dR_{i,j}^{[5]} = \prod_{i,j} N_i^i N_j^j$$  \hspace{1cm} A.3.7
Appendix 4: Proof of Volume Correction Factors for Discretization of Litster et al.

This proof shows that the choice of correction factors given in equations (3.3.14) meet the necessary requirements for conservation of the zeroth and third moments of the distribution.

\[
\frac{dm_0}{dt} = \frac{1}{2} \frac{1}{m_0^2} \tag{A.4.1}
\]

\[
\frac{dm_3}{dt} = 0 \tag{A.4.2}
\]

Equation 3.3.14 from the text:

\[
\frac{dm_3}{dt} = \sum_i v_i \frac{dN_i}{dt} = \sum_i v_i \left[ \frac{dN_i}{dt} \right]_{agg}
\]

\[
= \sum_i v_i \left[ \frac{i[S(q)]_i}{j} \frac{dN_i}{dt} \right]_{agg} + \sum_{k=2}^q \sum_{j=[S(q)+k]_k}^{[S(q)+k+1]_k} N_{i[k,j]} N_{i[k+1,j]} \left( \frac{2^{1/q} + 1}{2^{1/q} + 1} \right) - \frac{2^{(j/k+1)/q}}{2^{(j/k+1)/q} + C_2} + \frac{2^{(j/k+1)/q} + 1}{2^{(j/k+1)/q} + C_2} \tag{A.4.7}
\]
Appendix 4: (Continued)

In the brackets, the summation of terms 1 and 5 equal 0:

\[
\sum_{i=1}^{\delta(q)} \frac{1}{2^{1/q}} = 0 \quad \text{A.4.4}
\]

term 2 + term 3 =

\[
\sum_{k=2}^{q} \sum_{i=1}^{\delta(q)+1} \sum_{j=1}^{\delta(q)+2} i_{i,j} N_i N_j \quad \text{A.4.5}
\]

Finally, combining all terms:

\[
\frac{dm_0}{dt} = \sum_{i} \sum_{j=1}^{1/2} i_{i,j} N_i N_j = 0 \quad \text{A.4.6}
\]

Proof for the third moment using equation 3.3.14:

\[
\frac{dm_3}{dt} = \sum_{i} v_i \frac{dN_i}{dt} \quad \text{A.4.6}
\]
Appendix 4: (Continued)

\[
\frac{dN_j}{dt} = \sum_{j=1}^{i[S(q)]} N_i N_j \left( 2^{1/q} \sum_{j=1}^{2^{1/q}} 1 + 2^{(j/j+1)/q} + C_1 \right) + \sum_{k=2}^{q} \sum_{j=1}^{i[S(q)]} N_i N_{j+k} \left( 2^{1/q} \sum_{j=1}^{2^{1/q}} 1 + 2^{(j/j+1)/q} + C_2 \right) + \frac{1}{2} \sum_{k=2}^{q} \sum_{j=1}^{i[S(q)]} N_i N_{j+k} \left( 2^{1/q} \sum_{j=1}^{2^{1/q}} 1 + 2^{(j/j+1)/q} + C_3 \right)
\]

Adding terms 1 and 4 within the brackets yields:

\[
\frac{dm_3}{dt} = \sum_{j=1}^{i[S(q)]} N_i N_j 2^{(j/j+1)/q}
\]  \[A.4.8\]

Summing terms 2 and 3 yields:

\[
\frac{dm_2}{dt} = \sum_{k=2}^{q} \sum_{j=1}^{i[S(q)]} N_i N_{j+k} \left( 2^{(j/j+1)/q} + 1 \right)
\]

\[
\frac{dm_3}{dt} = \sum_{j=1}^{i[S(q)]} N_i N_j \left( 2^{(j/j+1)/q} + 1 \right)
\]  \[A.4.9\]

Summing terms 4, A.4.8, and A.4.9 yields:

\[
\frac{dm_5}{dt} = \sum_{j=1}^{i[S(q)]} N_i N_j 2^{(j/j+1)/q} \sum_{j=2}^{i[S(q)]} N_i N_j
\]  \[A.4.10\]
Appendix 4: (Continued)

Finally,

\[ \frac{dm_3}{dt} = v_i \sum_{j=1}^{N_i} 2^{(j/q) - 1/q} \sum_{j=1}^{N_j} \theta_i j N_i N_j \]

A.4.11

Remembering that \( 2^{i,j} = 2^{j,i} \), and \( \frac{v_{i+1}}{v_i} = 2^{1/q} \)

\[ \frac{dm_3}{dt} = 0 \]

A.4.12
Appendix 5: MATLAB Code for Mathematical Model

Population Balance Solution Program (pbesol.m)


%function [Iagg,momentserror]=pbesoltstperi(x)

% file used to set up and solve the Population Balance equations

% and solve them.

Hamaker=0.79e-20; %/*. Joules *//* Eff. Hamaker Const.

eps_i=80; %/*. Dielectric Const. medium

eps_o=8.854e-12; %/*. Dielectric Const. vac.

boltzmann=1.38044e-23; %/*. J/K */ Boltzmann Const.

viscosity=1.9e-4; %/*. Newton.sec/m2 */

e=1.6021917e-19; %/*. Coulombs */ /* electron charge

N_Avo=6.022169e23; %/*. 1/mol *//* Avogadro's Num.

l_c=1.0e-2; %/*. mole/m3 - Impurities Conc. */ (salt)[mole/m3]

t=293.15; % Temperature

%/*. Calculate debye length */

debye_length = sqrt(2.0*l_c*e*e*N_Avo/(eps_o*eps_i*boltzmann*t));
Appendix 5: (Continued)

%Input field:

%----------------------------------------------------------------

%Particle Diameter Range:

Ds=0.3E-6; %Smallest Diameter in discretization range

Dl=2.0E-6; %Largest Diameter in discretization range

% Enter discretizing quantity

global q;

q=6;

%----------------------------------------------------------------

%Calculate upper and lower volume;

Vs=4/3*pi*(Ds/2)^3;

Vl=4/3*pi*(Dl/2)^3;

%Calculate number of equations needed to cover range

global Z

Z=ceil((q/log(2))*log(Vl/Vs));

%Create the list of volumes;

Vm=Vs;
Appendix 5: (Continued)

for l = 1:Z,

\[ V(l) = \frac{V_s}{2}(l/q); \]

end

% calculate diameters;

\[ D = 2\left(\frac{V_s}{3/4}\pi\right)^{1/3}; \]

% Convert this to dimensionless length form;

\[ L = \left(\frac{V}{V_m}\right)^{1/3}; \]

% Calculate Do for later

\[ Do = \left(6\frac{V_m}{\pi}\right)^{1/3}; \]

% make the initial PSD;

% Create initial PSD

% for test purposes this will be given here but in reality

% this will be read from a file and the parameters in the

% INPUT field above will be calculated from the read file

%------------------------------------------

No = 1.475E+10; % part per ml from experiment initial condition;

mean = 0.503E-06; % mean of initial distr5.048908E-05

174
Appendix 5: (Continued)

\sigma = 0.0063\text{E}-6; \text{ std dev of initial dist;}

N = \text{zeros}(Z, 1);

\text{for } I = 1:Z,

\%N(I) = \text{gaussint('initialdist',D(I)*2^(-1/(2*3*q)),D(I)*2^1/(2*3*q)),500,mean,\sigma,\text{No);}

\%N(I) = \text{quad8('initialdist',D(I)*2^(-1/(2*3*q)),D(I)*2^1/(2*3*q)),[],[],mean,\sigma,\text{No);}

N = \text{No.*normpdf(D,\text{mean,}\sigma)/max(normpdf(D,\text{mean,}\sigma));}

\text{end}

\%in part cm^3

\%N = N.*1000; \text{ convert to part/cm^3}

Nd = N; \text{ save to look at}

\%---------------------------------------------------------------------

\%Create kernel equation;

\%---------------------------------------------------------------------

global F

F = \text{zeros}(Z);

global W

W = \text{zeros}(Z);
Appendix 5: (Continued)

global B

pot_a=zeros(Z,1);
pot_b=zeros(Z,1);
tot_e=zeros(Z,1);
h=zeros(Z,1);

%h=zeros(Z,1);

% constants for aggregation kernel

vis=1.001; %viscosity in cP

T=293.15; % Temperature

%h=linspace(5,500,Z).*1e-9;

%G=91;

for I=1:Z,

for J=1:Z,

    F(I,J)=cmperi(D(I),D(J),vis,T);

    [W(I,J),pot_a(I),pot_b(I),h(I),tot_e(I)]=main_repulsion(D(I),D(J));

    Dz(I)=D(I);

    Dx(J)=D(J);
Appendix 5: (Continued)

%B(I,J)=cmperi(D(I),D(J),vis,T)+cmdsed(D(I),D(J),vis,1.05,1);

%B(I,J)=emortho(D(I),D(J),G);

end

end

F=F.*1000000; %convert from m^3/s to cm^3/hr

%W=W.*1000000; %convert from m^3/s to cm^3/hr test

%-----------------------------------------------

%--Collision Mechanism----

figure(1);

mesh(Dz/1E-6,Dx/1E-6,log(F));

axis equal

axis normal

ht1=title('log of Perikinetic Collision Mechanism for HHF');

hx1=xlabel('Particle Diameter [micron]');

hy1=ylabel('Particle Diameter [micron]');

hz1=zlabel('Stability Ratio');

set([ht1,hx1,hy1,hz1],'units','normalized');
Appendix 5: (Continued)

set(gca,'Xscale','log','Yscale','log');

drawnow;

%--Stability Ratios----

figure(2);

mesh(Dz/1E-6,Dx/1E-6,log(W));

axis equal

axis normal

ht1=title('log of Stability Ratios');

hx1=xlabel('Particle Diameter [micron]');

hy1=ylabel('Particle Diameter [micron]');

hz1=zlabel('Stability Ratio');

set([ht1,hx1,hy1,hz1],'units','normalized');

set(gca,'Xscale','log','Yscale','log');

drawnow;

%-----------------------------------------------------

%Map of Aggregation Coefficient

%-----------------------------------------------------
Appendix 5: (Continued)

%ww=log(W)/100;

B=F./W;

figure(3);

mesh(Dz/1E-6,Dx/1E-6,log(B));

axis equal

axis normal

ht1=title('log of Aggregation Coefficient');

hx1=xlabel('Particle Diameter [micron]');

hy1=ylabel('Particle Diameter [micron]');

hz1=zlabel('Stability Ratio');

set([ht1,hx1,hy1,hz1],'units','normalized');

set(gca,'Xscale','log','Yscale','log');

drawnow;

%-----------------------------------------------

%Integration of the differential equation;

OPTIONS=odeset('RelTol',1e-4,'Stats','on');

TSPAN=[0 0.5 1 2 3 21.5 26];
Appendix 5: (Continued)

TSPAN=[0 0.5 1 2 3 4 5];

[T,Y]=ode45('diffvec',TSPAN,N,OPTIONS);

[linenum,K]=size(Y);

figure(4);
plot(T,Y);

%calculate lagg:

M0T0=moment(L,Y(1,:),0);

for I=1:linenum,

    lagg(I)=1-moment(L,Y(I,:),0)/M0T0;

end

%calculate Moments from data

for J=0:6,

    for I=1:linenum,

        resultmoments(J+1,I)=moment(L,Y(I,:),J)/moment(L,Y(1,:),J);

    end

end

Yn=Y;
Appendix 5: (Continued)

%fname=strcat('psdperi',num2str(q));
fname=strcat('psdq',num2str(q));
save(fname)
figure(5);
semilogx(D,Yn(1,:),D,Yn(2,:),D,Yn(3,:),D,Yn(4,:),D,Yn(5,:),D,Yn(6,:),D,Yn(7,:));
%axis([0 3 0 1.4]);
%hold on;

Main repulsion program (Originally created by Marquez (1994), updated by C. O’Brien (2003)

function [w1,pot_a,pot_b,h,tot_e]=main_repulsion(d1,d2)
Diam_o=0.01e-6; %diameter of smallest particle
epsilon=1.0e-5;  %/* Relative Error
hmin=1.0e-9; %/* Min integ. length for forces in stab.
pi=3.141592653589793; %/* Pi
Hamaker=0.79e-20; %/* Joules /* Eff. Hamaker Const.
eps_i=80;  %/* Dielectric Const. medium
eps_o=8.854e-12; %/* Dielectric Const. vac.

181
Appendix 5: (Continued)

boltzmann=1.38044e-23; %*/ J/K */ Boltzmann Const.

viscosity=1.001; %*/ Newton.sec/m2 */

e=1.6021917e-19; %*/ Coulombs */ */ electron charge

N_Avo=6.022169e23; %*/ 1/mol */ */ Avogadro's Num.

Ic=1.0e-2; %*/ mole/m3 - Impurities Conc. */ (salt)[mole/m3]

MAXIMO=90;

t=293.15;

cmap=zeros(1,50);

xmap=zeros(1,50);

s1=zeros(1,30);

wel=zeros(1,30);

% */ ********************************************************** */

for i = 1:MAXIMO-5;

    index(i) = i;

end

% */ ********************************************************** */

% */Define some relevant constants */
Appendix 5: (Continued)

%t = 308.0; /*Temperature */

/*believed to be conversion constants.*/

a4 = 0.2;

c = 1.0; c = c/135.0;

b1 = 16.0*c;

c = 1.0; c = c/12825.0;

b2 = 6656.0*c;

c = 1.0; c = c/56430.0;

b3 = 28561.0*c;

c = 1.0; c = c/50.0;

b4 = 9.0*c;

c = 1.0; c = c/55.0;

b5 = 2.0*c;

c_31 = 3.0*c;

c = 1.0; c = c/32.0;

c_32 = 3.0*c; c_33 = 9.0 *c;

c = 1.0; c = c/13.0;
c_41 = 12.0*c;

    c = 1.0; c = c/2197.0;

    c_42 = 1932.0*c; c_43 = 7200.0*c;

    c_44 = 7296.0*c;

    c = 1.0; c = c/216.0;

    a1 = 25.0*c;

    c_51 = 439.0*c;

    c = 1.0; c = c/513.0;

    c_52 = 3680.0*c;

    c = 1.0; c = c/4104.0;

    a3 = 2197.0*c;

    c_53 = 845.0*c;

    c_63 = 1859.0*c;

    c = 1.0; c = c/27.0;

    c_61 = 8.0*c;

    c = 1.0; c = c/2565.0;

    a2 = 1408.0*c;
Appendix 5: (Continued)

c_62 = 3544.0*c;

c = 1.0; c = c/40.0;

c_64 = 11.0*c;

% /* Roots for Gaussian Quadrature */

s1(1) = -0.993128599185094924786;

s1(2) = -0.963971927277913791268;

s1(3) = -0.912234428251325905868;

s1(4) = -0.839116971822218823395;

s1(5) = -0.746331906460150792614;

s1(6) = -0.636053680726515025453;

s1(7) = -0.510867001950827098004;

s1(8) = -0.373706088715419560673;

s1(9) = -0.227785851141645078080;

s1(10) = -0.076526521133497333755;

for i = 1:10

    s1(10+i) = -s1(10-i+1);

end % /* symetric about zero */
Appendix 5: (Continued)

% /* Weights for Gaussian Quadrature */

wel(1) = 0.017614007139152118312;
wel(2) = 0.040601429800386941331;
wel(3) = 0.062672048334109063570;
wel(4) = 0.083276741576704748725;
wel(5) = 0.101930119817240435037;
wel(6) = 0.118194531961518417312;
wel(7) = 0.131688638449176626898;
wel(8) = 0.142096109318382051329;
wel(9) = 0.149172986472603746788;
wel(10) = 0.152753387130725850968;

for i = 1:10

    wel(10+i) = wel(10-i+1); %/*symetric about zero */

end

% /* Surface potential scaling factor */

Cp = 0.6;
Appendix 5: (Continued)

Co = 6.25e-18*exp(15.71263054*Cp);

%Cp=0.0;

%/* Calculate debye length */

debye_length = sqrt(2.0*Ic*e*e*N_Avo/(eps_o*eps_i*boltzmann*t));

%fprintf(’ Debye Length = %10e\n ’,debye_length);

%fprintf(’ Cp = %4.2f Temp = %5.1fоС \n\n',Cp,(t - 273));

%fprintf(’ D1 D2 HHF SR OHW Rep Marquez SR\n\n’);

q_o = Co*exp(Cp*log(0.5*d1));

%q_o= Total Charge on particle enter in Coulombs*/

psi_do = q_o/4.0/pi/eps_i/eps_o/(0.5*d1); %/*Units are Volt*/

%/* Actual surface scaling portion*/

q2 = Co*exp(Cp*log(0.5*d2));

psi2 = q2/4.0/pi/eps_i/eps_o/(0.5*d2);

if psi_do > psi2

psimax = psi_do;

psimin = psi2;
Appendix 5: (Continued)

d1o=d1;

d2o=d2;

else

psimax = psi2;

psimin = psi_do;

d1o=d2;

d2o=d1;

end

psimax = psimax*e/boltzmann/t;

psimin = psimin*e/boltzmann/t;

cmin = -2.0*cosh(psimin); % minimum case

cmap(1)= cmin;

cmax2 = 10.0*cosh(psimax);

permiso = 0;

x_ref = sep_ref(psimax,psimin,cmin,permiso); % integrate eq. 6.41 by RKF monotonically

xmap(1) = x_ref;

xmin = xmap(1);
Appendix 5: (Continued)

xmap(41) = 5.0;

xmap(2) = (xmap(41)-xmap(1))*0.025;

for j=3:40

xmap(j) = (j-1)*xmap(2) + x_ref;
end

xmap(2) = xmap(2) + x_ref;

cmax = -2.0;

for j=2:41

xd = xmap(j);

c_der = cmax;

c_izq = cmin;

permiso = 0;

er1 = 10.0;

er2 = 10.0;

if (er1 > epsilon) & (er2 > 0.01*epsilon)

psi_o = 0;

x0 = 0.0;
Appendix 5: (Continued)

\[
xc = 0.0;
\]

\[
c = 0.5*(c_{\text{der}} + c_{\text{izq}});
\]

\[
[\text{psi}_0, x_0, xc, x_{\text{cen}}]=\text{sep\_placas}(\text{psimax}, \text{psimin}, c, \text{permiso}, xd);
\]

\[
\text{if } xc > xd
\]

\[
c_{\text{der}} = c;
\]

\[
\text{else}
\]

\[
c_{\text{izq}} = c;
\]

\[
\text{end}
\]

\[
er1 = \text{abs}(xd-xc);
\]

\[
er2 = \text{abs}(c_{\text{der}}-c_{\text{izq}});
\]

\[
\text{end } /* if */
\]

\[
cmap(j) = c;
\]

\[
cmin = c;
\]

\[
\text{end } /* next } j */
\]

\[
/* Map formed */
\]

\[
cmax2 = 10.0*\text{cosh}(\text{psimax});
\]

\[
cmin = cmap(1);
\]

190
Appendix 5: (Continued)

xmin = xmap(1);

xmax = xmin;

v1 = flat_ocfe(xmap(41),t,psimax,psimin,x_ref,cmap,cmax2,xd,xmax,cmin,xmap);

h1 = xmap(41);

cmax2 = 10.0*cosh(psimax);

cmin = cmap(1);

xmin = xmap(1);

v2 = flat_ocfe(xmap(35),t,psimax,psimin,x_ref,cmap,cmax2,xd,xmax,cmin,xmap);

h2 = xmap(35);

if d1o > d2o

[w1,w3,pot_a,pot_b,h,tot_e]=w_peri((0.5*d1o),(0.5*d2o),t,psimax,psimin,cmin,xmin,h1,h2,xd,x_ref);

else

[w1,w3,pot_a,pot_b,h,tot_e]=w_peri((0.5*d2o),(0.5*d1o),t,psimin,psimax,cmin,xmin,h1,h2,xd,x_ref);

end
Appendix 5: (Continued)

Calculation of Perikinetic Stability Ratios (w_peri.m) (Originally created by Marquez (1994), updated by C. O’Brien (2003))

function [w1,w3,pot_a,pot_b,h,tot_e]=w_peri(r1,r2,t,psi1,psi2,cmin,xmin,h1,h2,xd,x_ref)

%Calculation of Stability ratio

%define constants

epsilon=1.0e-5;  %/* Relative Error

hmin=1.0e-9;  %/* Min integ. length for forces in stab.

pi=3.141592653589793;  %/* Pi

Hamaker=0.79e-20;  %/* Joules /*/ Eff. Hamaker Const.

eps_i=80;  %/* Dielectric Const. medium

eps_o=8.854e-12;  %/* Dielectric Const. vac.

boltzmann=1.38044e-23;  %/* J/K  */ Boltzmann Const.

viscosity=1.001;  %/* Newton.sec/m2  */

r=1.6021917e-19;  %/* Coulombs  *//* electron charge

N_Avo=6.022169e23;  %/* 1/mol  *//* Avogadro's Num.

Ic=1.0e-2;  %/* mole/m3 - Impurities Conc.  */(/salt)[mole/m3]

%H=10:1000;  %H=H./1e9;
Appendix 5: (Continued)

debye_length = sqrt(2.0*Ic*e*e*N_Avo/(eps_o*eps_i*boltzmann*t)) ;

f1=zeros(1,20);

f2=zeros(1,20);

f3=zeros(1,20);

r=zeros(1,20);

s=zeros(1,25);

we=zeros(1,25);

s2=zeros(1,25);

we2=zeros(1,25);

% /* Integrate on the non-asymptotic region of the function */

s(1) = -1.0;

s(2) = -0.932469514203152;

s(3) = -0.661209386466265;

s(4) = -0.238619186083197;

for i = 1:4

s(4+i) = -s(4-i+1);
end

193
we(1) = 0.0;

we(2) = 0.171324492379170;

we(3) = 0.360761573048139;

we(4) = 0.467913934572691;

for i = 1:4
we(4+i) = we(4-i+1);
end

factor = 4.0*pi*r1*r2*1e*N_Avo*boltzmann*t/(r1+r2)/debye_length/debye_length;

integral1 = 0.0;

%integral2 = 0.0;

integral3 = 0.0;

%fprintf(' Psi1 = %f  Psi2 = %f \n',psi1,psi2);

%fprintf(' R1 = %f  R2 = %f \n',r1*debye_length,r2*debye_length);

%fprintf(' DL h  HHF Pot  OCFE Pot Marquez\n');

%fprintf(' =========== =========== =========== ===============\n');

nc = 6;

ho = 1.0e-9; %Minimum length : 10 angstroms
Appendix 5: (Continued)

\[ b = r_1 + r_2 + h_0; \]

for \( i = 1:6 \)

\[ h_0 = h_0 \times 3.0; \]

\[ a = b; \]

\[ b = b + h_0; \]

for \( j = 2:(n+1) \)

\[ r(j) = 0.5 \times ((b-a) \times s(j) + b + a); \]

\[ h = r(j) - (r1+r2); \]

\[ \text{pot}_a = \text{attraction}(r1,r2,h); \]

\[ \text{pot}_b = \text{hhf_rep}(r1,r2,h,t,\psi_1,\psi_2) \times \text{factor}; \]

\[ \text{dl}_r1 = \text{debye_length} \times r1; \]

\[ \text{dl}_r2 = \text{debye_length} \times r2; \]

\[ \text{dl}_h = \text{debye_length} \times h; \]

\[ \text{dl}_\psi1 = \psi1; \]

\[ \text{dl}_\psi2 = \psi2; \]

\[ [p1,p2]=\text{field_potoc2}(\text{dl}_r1,\text{dl}_r2,\text{dl}_\psi1,\text{dl}_\psi2,\text{dl}_h,t,cmin,xmin,v1,v2,h1,h2,xd,x_{\text{ref}}); \]
tot_e=(pot_a + pot_b);

%pot_c = p1;

pot_d = p2;

pot_c =pot_c .* factor;

pot_d = pot_d .* factor;

ar = (pot_a + pot_b)./t./boltzmann;

f1(j) = exp(ar)/(r(j).*r(j));

%ar = (pot_a + pot_c)./t./boltzmann;

%f2(j) = exp(ar)./(r(j).*r(j));

ar = (pot_a + pot_d)./t./boltzmann;

f3(j) = exp(ar)./(r(j).*r(j));

%fprintf(' %10e %10e %10e %10e \n',dl_h,pot_b,pot_c,pot_d);

end % % Next j

par_int = 0.0;

for j = 2:(nc+1)

    par_int = par_int + we(j).*f1(j);

    integral1 = integral1 + 0.5*(b-a).*par_int;
Appendix 5: (Continued)

par_int = 0.0;

end

%for j = 2:(nc+1)

%  par_int = par_int + we(j).*f2(j);

%integral2 = integral2 + 0.5*(b-a).*par_int;

% par_int = 0.0;

%end

for j = 2:(nc+1)

par_int = par_int + we(j).*f3(j);

integral3 = integral3 + 0.5.*(b-a).*par_int;

end

end  %}  /* Next i */

%/* Integrate on the asymptotic region of the function */

% /*Laguerre roots and weights.*/

s2(1) = 0.093307812017;

s2(2) = 0.492691740302;

s2(3) = 1.215595412071;
Appendix 5: (Continued)

s2(4) = 2.269949526204;

s2(5) = 3.667622721751;

s2(6) = 5.425336627414;

s2(7) = 7.565916226613;

s2(8) = 10.120228568019;

s2(9) = 13.130282482176;

s2(10) = 16.654407708330;

s2(11) = 20.776478899449;

s2(12) = 25.623894226729;

s2(13) = 31.407519169754;

s2(14) = 38.530683306486;

s2(15) = 48.026085572686;

we2(1) = 0.218234885940;

we2(2) = 0.342210177923;

we2(3) = 0.263027577942;

we2(4) = 0.126425818106;

we2(5) = 0.0402068649210;
Appendix 5: (Continued)

\[
\begin{align*}
\text{we2}(6) &= 0.00856387780361; \\
\text{we2}(7) &= 0.00121243614721; \\
\text{we2}(8) &= 0.000111674392344; \\
\text{we2}(9) &= 0.645992676202e-5; \\
\text{we2}(10) &= 2.22631690710e-7; \\
\text{we2}(11) &= 4.22743038498e-9; \\
\text{we2}(12) &= 3.92189726704e-11; \\
\text{we2}(13) &= 1.45651526407e-13; \\
\text{we2}(14) &= 1.48302705111e-16; \\
\text{we2}(15) &= 1.60059490621e-20;
\end{align*}
\]

\[
\begin{align*}
\text{integral1} &= (r1+r2)\text{integral1}; \\
\%\text{integral2} &= (r1+r2)\text{integral2}; \\
\text{integral3} &= (r1+r2)\text{integral3}; \\
\text{w1} &= \text{integral1}; \\
\%\text{w2} &= \text{integral2}; 
\end{align*}
\]
Appendix 5: (Continued)

\[ w3 = \text{integral3}; \]

\texttt{aggdiff.m} (Originally written by Scott Fisher (1998), modified by C. O’Brien (2003))

function ret=aggdiff(t,N,I)

% differential for growth \( t \) is time, \( N \) is the population

% \( I \) is the index

%define globals which should be in place

global Z B q;

%initialize summation terms;

S1=0;

S2=0;

S3=0;

S4=0;

S5=0;

S6=0;

%build aggregation terms

%S1

for J=1:(I-S(1)),

200
if (((I-1)<1)\(\&\&(J<1))

\[ S_1 = S_1; \]

else

\[ S_1 = S_1 + (B(I-1,J)\times N(I-1)\times N(J)\times (2^{(J-I+1)/q})/2^{(1/q)-1}); \]

end

end

%S2

for P=2:q,

for J=(I-S(P-1)):I-S(P)),

if (((I-P)<1)\(\&\&(J<1))

\[ S_2 = S_2; \]

else

\[ S_2 = S_2 + (B(I-P,J)\times N(I-P)\times N(J)\times (2^{(J-I+1)/q})-1+2^{(-P-1)/q})/2^{(1/q)-1}); \]

end

end

end

%S3
Appendix 5: (Continued)

if (I-q)<1

$S_3=S_3$;

else

$S_3=((1/2)*B(I-q,I-q)*N(I-q)^2)$;

end

%S4

for P=1:(q-1),

for J=((I+1)-S(P)):(((I+1)-S(P+1)),”

if (((I-P)<1)|(J<1))

$S_4=S_4$;

else

$S_4=S_4+(B(I-P,J)*N(I-P)*N(J)*((-2^((J-I)/q)+2^((1/q)-2^((-P)/q)))/(2^((1/q)-1)))$;

end

end

end

%S5

for J=1:(I-S(1)+1),
Appendix 5: (Continued)

if ((I<1)&&(J<1))

    S5=S5;

else

    S5=S5+(B(I,J)*N(I)*N(J)*((2^((J-I)/q))/(2^(1/q)-1)));

end

end

%S6

for J=(I-S(1)+2):(Z),

    if ((I<1)&&(J<1))

        S6=S6;

    else

        S6=S6+(B(I,J)*N(I)*N(J));

    end

end

%fprintf('%s1,s2,s3,s4,s5,s6: %12.10e %12.10e %12.10e %12.10e %12.10e %12.10e
\n',S1,S2,S3,S4,S5,S6);

ret=S1+S2+S3+S4-S5-S6;
Appendix 5: (Continued)

attraction.m (Hamaker Calculation for van der Waals Forces)


function ret=attraction(r1,r2,h)

    Hamaker=0.79e-20;  %/* Eff. Hamaker Const.
    %/* NOTICE : r1,r2,h may be expressed in any units */

    den1 = h.*(h + (2.0.*(r1 + r2)));

    den2 = den1 + (4.0.*r1.*r2);

    ret= (-Hamaker*(((2.0.*r1.*r2)./den1) + ((2.0.*r1.*r2)./den2)+(log(den1./den2))./6.0));

avgD.m (Originally written by Scott Fisher (1998), modified by C. O’Brien (2003))

lb=15;  %set this number on where to break the distribution

for I=1:linenum,

    %volume average

    %Vavg(I)=sum(4./3.*pi.*((D/2).^3).*Yn(I,;))/sum(Y(I,:));

    %Vavg1(I)=sum(4./3.*pi*((D(lb)/2).^3).*Yn(I,1:lb))/sum(Y(I,1:lb));

    %Vavg2(I)=sum(4/3*pi*((D(up:length(D))/2).^3).*Yn(I,up:length(D)))./sum(Y(I,up:length(D)));

    %Vavg=2.*((Vavg.*(3/4/pi)).^(1/3));

    %Vavg=2.*(Vavg.*(3/4/pi)).^(1/3));
 Appendix 5: (Continued)

```matlab
%Vavg1=2.*((Vavg1.*(3/4/pi)).^(1/3));

%Vavg2=2.*((Vavg2.*(3/4/pi)).^(1/3));

%Davg(I)=(Mavg*3/1.05/4/pi).^(1/3)*2;

%length average
Davg(I)=sum(Dn.*Yn(I,:))/sum(Y(I,:));

temp=find(Dn<=Davg(I));

%lb=ceil((temp(1)+length(Dn))/2);

lb=temp(length(temp));

up=lb;

Davg1(I)=sum(Dn(1:lb).*Yn(1,1:lb))./sum(Y(1,1:lb));

Davg2(I)=sum(Dn(up:length(D))).*Yn(1,up:length(D)))./sum(Y(1,up:length(D)));

end

Davg1=polyval(polyfit(TSPAN,Davg1,3),TSPAN);

Davg2=polyval(polyfit(TSPAN,Davg2,3),TSPAN);


function ret=ceortho(D)
```

205
Appendix 5: (Continued)

% Calculation of Stability ratio

%d = diameter of agglomerate
%a = primary particle size

a = 0.102e-6;

% calculate radius
% a0 = d0/2;

% calculate number of primaries at each diameter
% a = ((D./2).^3)/(a0^3);

term1 = 2.1/((log(D./2*a))^0.29);

term2 = (((D./2*a)^0.075)-0.2)^3/2;

ret = term1*term2;

Differential Sedimentation (cmdsed.m)


function ret = cmdsed(D1,D2,vis,ps,p)

%m-file to calculate differential settling collision rate constant

% units needed

%D1, D2 -- meters
Appendix 5: (Continued)

%vis  -- cP

%ps,p  -- Kg/m^3  Ps-density of solid, p density of fluid

%gravitational constant

g=9.80665; %m/s^2

%calculate it

ret1=(2*pi*g/(9*vis*0.001))*(ps-p)*((D1/2+D2/2).^3).*(D1-D2);

ret=abs(ret1);

Orthokinetic Collision Mechanism (cmorth0.m)


function ret=cmorth0(D1,D2,G)

%m-file to calculate orthokinetic collision rate constant

%units needed

%D1,D2 -- meters

% G  -- 1/s  average shear rate

%calculate it

ret=(4/3)*G*((D1/2+D2/2).^3);
Appendix 5: (Continued)

Perikinetic Collision Mechanism (cmperi.m)


function ret=cmperi(D1,D2,vis,T)

%m-file to calculate perikinetic collision rate constant

%units needed

%D1,D2 -- meters

%vis -- cP

%T-- Kelvin

%define constants

kb=1.38066E-23; %J/K

%calculate it

%ret=(2/3)*(kb*T/(vis*0.001))*((D1/2+D2/2).^2)/(D1.*D2/4);
ret=(1/3)*(kb*T/(vis*0.001))*((D1/2+D2/2).^2)/(D1.*D2/4);

control.m (Originally written by E. Marquez (1994), modified by C. O’Brien (2003))

function ret=control(x,c)

if (2.0*cosh(x) + c) >= 0.0
    ret=1;
Appendix 5: (Continued)

else

    ret=0;

end

d2fracd.m (Originally written by S. Fisher (1998), modified by C. O’Brien (2003))

function ret=d2fracd(D,Df,psi,d0)

%calculate radius

a0=d0/2;

%calculate number of primaries at each diameter

numi=((D./2).^3)./(a0.^3);

%relation from Kuster

for I=1:length(D),

    if (numi(I)>1.2 & numi(I)<2.8)

        Dn(I)=2*1.8*a0;

    else

        Dn(I)=2*a0*(numi(I)./psi).^(1/Df);

    end

end
Appendix 5: (Continued)

ret=Dn;

diffvec.m (Originally written by E. Marquez (1994), modified by C. O’Brien (2003))

function ret=diffvec(t,N)

%function to build the vector for the differential equation

%solver to use;

global Z;

for I=1:(Z),

    temp(I)=aggdiff(t,N,I);

end

%fprintf('temp: %12.10e \n',temp);

ret=temp';

f.m (Originally written by E. Marquez (1994), modified by C. O’Brien (2003))

function ret=f(t,psi,c)

arg = 2.0*cosh(psi) + c;

if (arg < 0)

    fprintf (' message = %2d arg f = %10f\n',message,arg);

end
ret= -sqrt(arg);

f2.m (Originally written by E. Marquez (1994), modified by C. O’Brien (2003))

function ret=f2(t,psi,c)

    arg = 2.0*cosh(psi) + c;

    if (arg < 0)
        fprintf (‘ message = %2d arg f2 = %10f\n’,message,arg);
    end

    ret = sqrt(arg);

hhfrep.m (Originally written by E. Marquez (1994), modified by C. O’Brien (2003))

%file used to calculate hhf_repulsion

function ret=hhf_rep(r1,r2,h,t,psi1,psi2)

    pi=3.141592653589793; /* Pi

    eps_i=80;  /* Dielectric Const. medium

    eps_o=8.854e-12; /* Dielectric Const. vac.

    boltzmann=1.38044e-23; /* J/K */ Boltzmann Const.

    e=1.6021917e-19; /* Coulombs */ /* electron charge

    N_Avo=6.022169e23; /*/mol *//* Avogadro's Num.
Appendix 5: (Continued)

IC=1.0e-2; %/* mole/m3 - Impurities Conc. */ (salt)[mole/m3]

debye_length = sqrt(2.0*1e*eps*N_Avo/(eps_o*eps_i*boltzmann*t));

ys1 = psi1;
ys2 = psi2;

yp = 0.5*(ys1 + ys2);

y_ = 0.5*(ys1 - ys2);

term1 = (yp*yp)*log(1.0 + exp(-debye_length*h)) + (y_*y_)*log(1.0-exp(debye_length*h));

ret = term1* 2.0;

modelcomp.m (Originally written by S. Fisher (1998), modified by C. O’Brien (2003))

%model compare

%plot diameters

plotdiam;

load psdq6;

%load psdq4co;

%convert fractional dimension

Dn=d2fracd(D,1.71,0.503e-6);
Appendix 5: (Continued)

%Dn = D;

avgd;

hold on;

plot(TSPAN,Davg./1e-6,'k-');

plot(TSPAN,Davg1./1e-6,'k:');

plot(TSPAN,Davg2./1e-6,'k--');

load psdq6stco;

Dn = d2fracd(D,1.7,1,0.503e-6);

%Dn = D;

avgd;

hold on;

plot(TSPAN,Davg./1e-6,'r-');

plot(TSPAN,Davg1./1e-6,'r:');

plot(TSPAN,Davg2./1e-6,'r--');

%axis([0 5 0 1.4]);

legend('EXP Davg','EXP D1','EXP D2','SF MODEL Davg','SF MODEL D1','SF MODEL D2','MODEL Davg','MODEL D1','MODEL D2',2)
Appendix 5: (Continued)

moment.m (Originally written by S. Fisher (1998), modified by C. O’Brien (2003))

function ret=moment(L,Y,mom)

%for size-independent

r=L(2)/L(1);
ret=sum(((1+r)/2).*L.^mom).*Y);

%for size dependent

%ret=trapz(L,L.^mom.*Y);

plotdiam.m (Originally written by S. Fisher (1998), modified by C. O’Brien (2003))

% mfile to plot particle sizes for Exp C

load sp.dat;
X1=sp;

%plot(TSPAN,Davg/1e-6,'b-';TSPAN,Davg1/1e-6,'r-';TSPAN,Davg2/1e-6,'g-')

%hold on

plot(X1(:,1),X1(:,2)/1e-4,'ko')

hold on;

plot(X1(:,1),X1(:,4)/1e-4,'kv')

plot(X1(:,1),X1(:,6)/1e-4,'kd')

214
Appendix 5: (Continued)

xlabel('Time [hr'])

ylabel('Particle Diameter [micron'])

title('Particle Diameter versus Time')

S.m (Originally written by S. Fisher (1998), modified by C. O’Brien (2003))

function ret=S(x)

global q;

ret=floor(1-(q*log(1-2^(-x/q))/log(2)));

sep_mon.m (Originally written by E. Marquez (1994), modified by C. O’Brien (2003))

function ret=sep_mon(psi1,psi2,c,permiso,xd)

  epsilon=1.0e-5;  %/* Relative Error

  hmax = 5.0e-3;

  h = hmax;

  u2 = psi1;

  psi = psi1;

  x = 0.0;

  valido = 1;

  a4 = 0.2;
Appendix 5: (Continued)

\[ g = 1.0; \ g = g/135.0; \]

\[ b1 = 16.0* g; \]

\[ g = 1.0; \ g = g/12825.0; \]

\[ b2 = 6656.0* g; \]

\[ g = 1.0; \ g = g/56430.0; \]

\[ b3 = 28561.0* g; \]

\[ g = 1.0; \ g = g/50.0; \]

\[ b4 = 9.0* g; \]

\[ g = 1.0; \ g = g/55.0; \]

\[ b5 = 2.0* g; \]

\[ c_{31} = 3.0* g; \]

\[ g = 1.0; \ g = g/32.0; \]

\[ c_{32} = 3.0* g; \ c_{33} = 9.0 * g; \]

\[ g = 1.0; \ g = g/13.0; \]

\[ c_{41} = 12.0* g; \]

\[ g = 1.0; \ g = g/2197.0; \]

\[ c_{42} = 1932.0* g; \ c_{43} = 7200.0* g; \]
Appendix 5: (Continued)

c_{44} = 7296.0\times g;

g = 1.0; \ g = g/216.0;

a1 = 25.0\times g;

c_{51} = 439.0\times g;

g = 1.0; \ g = g/513.0;

c_{52} = 3680.0\times g;

g = 1.0; \ g = g/4104.0;

a3 = 2197.0\times g;

c_{53} = 845.0\times g;

c_{63} = 1859.0\times g;

g = 1.0; \ g = g/27.0;

c_{61} = 8.0\times g;

g = 1.0; \ g = g/2565.0;

a2 = 1408.0\times g;

c_{62} = 3544.0\times g;

g = 1.0; \ g = g/40.0;

c_{64} = 11.0\times g;
Appendix 5: (Continued)

if (permiso == 1 )

fprintf('error 1 in sep_mon: %9.6f %10.8f %10.8f\n', x, psi, f(x, psi, c));

end

if absval(psi-psi2) >= epsilon & (valido == 1)

if psi > psi2

/* 1 */

k1 = h*f(x, psi, c);

xo = x + 0.25*h;

u = psi + 0.25*k1;

if u > psi2

/* 2 */

k2 = h*f(xo, u, c);

xo = x + c_31*h;

u = psi + c_32*k1 + c_33*k2;

if u > psi2

/* 3 */

k3 = h*f(xo, u, c);
xo = x + c_41*h;

u = psi + c_42*k1 - c_43*k2 + c_44*k3;

if u > psi2

%/* 4 */

k4 = h*f(xo,u,c);

xo = x + h;

u = psi + c_51*k1 - 8.0*k2 + c_52*k3 - c_53*k4;

if u > psi2

%/* 5 */

k5 = h*f(xo,u,c);

xo = x + 0.5*h;

u = psi - c_61*k1 + 2.0*k2 - c_62*k3 + c_63*k4 - c_64*k5;

if u > psi2

%/* 6 */

k6 = h*f(xo,u,c);

r = absval(k1/360.0 - 128.0*k3/4275.0 - 2197.0*k4/75240.0 + k5/50.0 + 2.0*k6/55.0);

if r < epsilon/514.19

219
Appendix 5: (Continued)

er_in = 4.5;

else er_in = 0.84*sqrt(sqrt((epsilon/r))); 

end

if r < epsilon

u1 = psi + a1*k1 + a2*k3 + a3*k4 - a4*k5;

if control(u1,c)==1

*/ 7 */

psi = u1;

x = x+h;

u2 = f(x,psi,c);

if (permiso == 1)

fprintf('sep_mon error 2: %9.6f %10.8f %10.8f %10.8f %10.8f %10.8f
',x,psi,u2,er_in,r,h);

end

if er_in < 0.1

h = h*0.1;

else if er_in > 4.0

...
Appendix 5: (Continued)

h = h*4.0;

else h = h*er_in;

end

end /* 7 */

else h = h*0.1;

end

else h = h*0.1;

if (h < hmin)

fprintf('sep_mon error 3: h < hmin.!!!\n');

valido = 0;

end

end /* 6 */

else h = h*0.1;

end /* 5 */

else h = h*0.1;

end /* 4 */

else h = h*0.1;
Appendix 5: (Continued)

end /* 3 */

else h = h*0.1;

end /* 2 */

else h = h*0.1;

end /* 1 */

else h = h*0.1;

end

if h > hmax

h = hmax;

end

end /* End While */

ret=x;

sep_placas.m (Originally written by E. Marquez (1994), modified by C. O’Brien (2003))

function [psi_o,x0,xc,x_cen]=sep_placas(psi1,psi2,c,permiso,xd)

a4 = 0.2;

g = 1.0; g = g/135.0;
Appendix 5: (Continued)

\[ b_1 = 16.0 \cdot g; \]
\[ g = 1.0; \ g = g/12825.0; \]
\[ b_2 = 6656.0 \cdot g; \]
\[ g = 1.0; \ g = g/56430.0; \]
\[ b_3 = 28561.0 \cdot g; \]
\[ g = 1.0; \ g = g/50.0; \]
\[ b_4 = 9.0 \cdot g; \]
\[ g = 1.0; \ g = g/55.0; \]
\[ b_5 = 2.0 \cdot g; \]
\[ c_{31} = 3.0 \cdot g; \]
\[ g = 1.0; \ g = g/32.0; \]
\[ c_{32} = 3.0 \cdot g; \ c_{33} = 9.0 \cdot g; \]
\[ g = 1.0; \ g = g/13.0; \]
\[ c_{41} = 12.0 \cdot g; \]
\[ g = 1.0; \ g = g/2197.0; \]
\[ c_{42} = 1932.0 \cdot g; \ c_{43} = 7200.0 \cdot g; \]
\[ c_{44} = 7296.0 \cdot g; \]
Appendix 5: (Continued)

\[ g = 1.0; \ g = g/216.0; \]
\[ a1 = 25.0*g; \]
\[ c_51 = 439.0*g; \]
\[ g = 1.0; \ g = g/513.0; \]
\[ c_52 = 3680.0*g; \]
\[ g = 1.0; \ g = g/4104.0; \]
\[ a3 = 2197.0*g; \]
\[ c_53 = 845.0*g; \]
\[ c_63 = 1859.0*g; \]
\[ g = 1.0; \ g = g/27.0; \]
\[ c_61 = 8.0*g; \]
\[ g = 1.0; \ g = g/2565.0; \]
\[ a2 = 1408.0*g; \]
\[ c_62 = 3544.0*g; \]
\[ g = 1.0; \ g = g/40.0; \]
\[ c_64 = 11.0*g; \]
\[ hmax = 5.0e-3; \]
Appendix 5: (Continued)

h = hmax;

u2 = psi1;

psi = psi1;

x = 0.0;

epsilon = 1.0e-5; %/* Relative Error

if permiso == 1

fprintf('Error in sep_placas: %9.6f %10.8f %10.8f\n', x, psi, f(x, psi, c));

end

valido = 1;

%if ((absval(u2) >= epsilon) & (absval(psi-psi2) > epsilon) & (valido == 1))

if (abs(u2) >= epsilon) & (valido == 1)

if control(psi, c) == 1

%{ /* 1 */

k1 = h*f(x, psi, c);

xo = x + 0.25*h;

u = psi + 0.25*k1;
Appendix 5: (Continued)

if control(u,c) == 1

% { /* 2 */

k2 = h*f(xo,u,c);

xo = x + c_31*h;

u = psi + c_32*k1 + c_33*k2;

if control(u,c) == 1

% { /* 3 */

k3 = h*f(xo,u,c);

xo = x + c_41*h;

u = psi + c_42*k1 - c_43*k2 + c_44*k3;

if control(u,c) == 1

% { /* 4 */

k4 = h*f(xo,u,c);

xo = x + h;

u = psi + c_51*k1 - 8.0*k2 + c_52*k3 - c_53*k4;

if control(u,c) == 1

% { /* 5 */


Appendix 5: (Continued)

\[ k5 = h*f(xo,u,c); \]

\[ xo = x + 0.5*h; \]

\[ u = psi - c_61*k1 + 2.0*k2 - c_62*k3 + c_63*k4 - c_64*k5; \]

if ( absval(u) > 705.0)

fprintf('Error in sep_placas: u = %10f h = %10f xo = %10f x = %10f\n',u,h,xo,x);

%message = 6;

end

if control(u,c)==1

% { /* 6 */

k6 = h*f(xo,u,c);

r = absval(k1/360.0 - 128.0*k3/4275.0 - 2197.0*k4/75240.0 + k5/50.0 + 2.0*k6/55.0);

if r < (epsilon/514.19)

er_in = 4.5;

else

er_in = 0.84*sqrt(sqrt((epsilon/r)));

end

if r < epsilon
Appendix 5: (Continued)

\[ u_1 = \psi + a_1 k_1 + a_2 k_3 + a_3 k_4 - a_4 k_5; \]

if control(u1,c)==1

\% { /* 7 */

\[ \psi = u_1; \]

\[ x = x + h; \]

\[ u_2 = f(x,\psi,c); \]

if (permiso == 1)

\[ \text{fprintf('Error in sep_placas: } \%9.6f \%10.8f \%10.8f \%10.8f \%10.8f \%10f}'\n\]

',x,psi,u2,er_in,r,h);

\] end

if er_in < 0.1

\[ h = h * 0.1; \]

else if er_in > 4.0

\[ h = h * 4.0; \]

else h = h * er_in;

end

\] end */ 7 */
Appendix 5: (Continued)

else

    h = h * 0.1;

end %}

else h =h * 0.1;

    if (h < hmin)

        fprintf('Error in sep_placas: h < hmin.!!\n');

        valido = 0;

    end

end %} /* 6 */

else h =h * 0.1;

end %} /* 5 */

else h = h*0.1;

end %} /* 4 */

else h =h * 0.1;

end %} /* 3 */

else h =h * 0.1;

end %} /* 2 */
else h = h * 0.1;
end %} /* 1 */
else h = h * 0.1;
end
if h > hmax

h = hmax;
end %} /* End While */
end

psi_o = psi;

if psi1 > psi2

x_sum = sep_mon(psi1,psi2,c,permiso,xd);
else x_sum = 0.0;
end

x0 = x + x_sum;

xc = 2.0.*x + x_sum;

x_cen=2.0.*x + x_sum;

%psi_o=dir1;
Appendix 5: (Continued)

%!x0=dir2;

%!xc=dir3;

%!x_cen=dir3;

%fprintf('xc in sep_placas: %f
', xc);

sep_ref.m (Originally written by E. Marquez (1994), modified by C. O’Brien (2003))

function ret=sep_ref(psi1,psi2,c,permiso)

    a4 = 0.2;

    g = 1.0; g = g/135.0;

    b1 = 16.0*g;

    g = 1.0; g = g/12825.0;

    b2 = 6656.0*g;

    g = 1.0; g = g/56430.0;

    b3 = 28561.0*g;

    g = 1.0; g = g/50.0;

    b4 = 9.0*g;

    g = 1.0; g = g/55.0;

    b5 = 2.0*g;
Appendix 5: (Continued)

c_31 = 3.0\times g;

g = 1.0; \ g = g/32.0;

c_32 = 3.0\times g; \ c_33 = 9.0 \times g;

g = 1.0; \ g = g/13.0;

c_41 = 12.0\times g;

g = 1.0; \ g = g/2197.0;

c_42 = 1932.0\times g; \ c_43 = 7200.0\times g;

c_44 = 7296.0\times g;

g = 1.0; \ g = g/216.0;

a1 = 25.0\times g;

c_51 = 439.0\times g;

g = 1.0; \ g = g/513.0;

c_52 = 3680.0\times g;

g = 1.0; \ g = g/4104.0;

a3 = 2197.0\times g;

c_53 = 845.0\times g;

c_63 = 1859.0\times g;
Appendix 5: (Continued)

g = 1.0; g = g/27.0;

c_61 = 8.0*g;

g = 1.0; g = g/2565.0;

a2 = 1408.0*g;

c_62 = 3544.0*g;

g = 1.0; g = g/40.0;

c_64 = 11.0*g;

hmax = 5.0e-3;

h = hmax;

u2 = psi1;

psi = psi1;

x = 0.0;

epsilon=1.0e-5;  /* Relative Error

if permiso == 1

    fprintf('sep_ref error 1: %9.6f %10.8f %10.8f
',x,psi,f(x,psi,c));

end

valido = 1;
Appendix 5: (Continued)

if ((abs(u2) >= epsilon) & (abs(psi-psi2) > epsilon) & (valido ==1) )

\%

if control(psi,c) == 1

\%

% { /* 1 */

k1 = h*f(x,psi,c);

xo = x + 0.25*h;

u = psi + 0.25*k1;

if control(u,c) ==1

% { /* 2 */

k2 = h*f(xo,u,c);

xo = x + c_31*h;

u = psi + c_32*k1 + c_33*k2;

if control(u,c)==1

% { /* 3 */

k3 = h*f(xo,u,c);

xo = x + c_41*h;

u = psi + c_42*k1 - c_43*k2 + c_44*k3;

234
Appendix 5: (Continued)

if control(u,c)==1

% { /* 4 */

k4 = h*f(xo,u,c);

xo = x + h;

u = psi + c_51*k1 - 8.0*k2 + c_52*k3 - c_53*k4;

if control(u,c)==1

% { /* 5 */

k5 = h*f(xo,u,c);

xo = x + 0.5*h;

u = psi - c_61*k1 + 2.0*k2 - c_62*k3 + c_63*k4 - c_64*k5;

if control(u,c)==1

% { /* 6 */

k6 = h*f(xo,u,c);

r = abs(k1/360.0 - 128.0*k3/4275.0 - 2197.0*k4/75240.0 + k5/50.0 + 2.0*k6/55.0);

if r < (epsilon/514.19)

er_in = 4.5;

else

235
Appendix 5: (Continued)

er_in = 0.84*sqrt(sqrt((epsilon/r)));

    end

if r < epsilon

    if control(u1,c)==1

        psi = u1;
        x = x + h;
        u2 = f(x,psi,c);

        if (permiso == 1)

            fprintf('se_r error 2: %9.6f %10.8f %10.8f %10.8f %10.8f %10f\n',x,psi,u2,er_in,r,h);

        end

    end

    if er_in < 0.1

        h = h * 0.1;

    else if er_in > 4.0

        }
Appendix 5: (Continued)

h = h * 4.0;

else h = h * er_in;

end

dend %}/* 7 */

else

h = h * 0.1;

dend %}
Appendix 5: (Continued)

else h =h * 0.1;
end */ 3 */
else h =h * 0.1;
end */ 2 */
else h =h * 0.1;
end */ 1 */
else h =h * 0.1;
end

if h > hmax
    h = hmax;
end */ End While */
end

ret=x;

flat_ocfe.m (Originally written by E. Marquez (1994), modified by C. O’Brien (2003))

function ret=flat_ocfe(h,t,psi1,psi2,x_ref,cmpx2,cmx,x3,xd,xmin,cmin,xmap)

epsilon=1.0e-5;  %/* Relative Error
Diam_o=0.01e-6;
Appendix 5: (Continued)

Q=1;
Z=20;
e=1.6021917e-19;
boltzmann=1.38044e-23;
%cmap=zeros(1,50);
%xmap=zeros(1,50);
xmax=xmin;

%Begin flat_ocfe%%%
if psi2 > psi1
    psi_temp = psi2;
    psi2 = psi1;
    psi1 = psi_temp;
end
if h <= x_ref
    caso = 0;
else caso = 1; % caso almost always =1
end
Appendix 5: (Continued)

```c
%fprintf("caso: %e \n",caso);

er1 = 10.0;

er2 = 10.0;

permiso = 0;

if caso ==1

    xmax=xmap(1);

    cmax = cmap(1);

    i = 1;

    if (h>xmax)\&(i<=41)

        i=i+1;

        xmax=xmap(i);

        cmax=cmap(i);

    end

if xmax > xmap(41)

    fprintf('Error 1 in flat_ocfe: h > xmax!!!\n');

end

c_der = cmax;
```
Appendix 5: (Continued)

\[ \text{x\textsubscript{der}} = \text{ymax}; \]
\[ \text{c\textsubscript{izq}} = \text{cmin}; \]
\[ \text{x\textsubscript{izq}} = \text{xmin}; \]
\[ \text{c\textsubscript{cen}} = 0.5*(\text{c\textsubscript{der}} + \text{c\textsubscript{izq}}); \]
\[ \text{psi\textsubscript{o}} = 0; \]
\[ \text{x}0 = 0.0; \]
\[ \text{xc} = 0.0; \]
\[ \%\text{dir}1 = \text{psi\textsubscript{o}}; \]
\[ \%\text{dir}2 = \text{x}0; \]
\[ \%\text{dir}3 = \text{c\textsubscript{cen}}; \]
\[ \text{permiso} = 0; \]

\[ [\text{psi\textsubscript{o}}, \text{x}0, \text{xc}, \text{c\textsubscript{cen}}] = \text{sep\_placas} (\text{psi1}, \text{psi2}, \text{c\textsubscript{cen}}, \text{permiso}, \text{xd}); \]
\[ \%\text{/}put \text{xd} \text{in} \text{here} \text{because} \text{there} \text{was} \text{no} \text{argument}^{*}/ \]
\[ \%\text{fprintf} ('\text{dir\_mat: \%f \%f \%f \n}', \text{psi\textsubscript{o}}, \text{x}0, \text{xc}); \]
\[ \\text{nit} = 0; \]
\[ \text{if} (\text{er}1 > \text{epsilon}) \& (\text{er}2 > 0.01*\text{epsilon}) \]
\[ \\text{nit} = \text{nit} + 1; \]
Appendix 5: (Continued)

opción = 1;

if ( absval(c_cen-c_izq) > 1.0e-6 ) & ( absval(c_izq-c_der) > 1.0e-6 ) & ( absval(c_der-c_cen) > 1.0e-6 )

al = ((x_der-x_izq)/(c_der-c_izq)-(x_cen-x_izq)/(c_cen-c_izq))/(c_der-c_cen);

    al=al+(al==0)*eps;

    be = (x_cen-x_izq)/(c_cen-c_izq) - al*(c_cen+c_izq);

    be=be+(be==0)*eps;

    ga = x_izq - al*c_izq*c_izq - be*c_izq;

else opcion = 0;

eend

if opcion == 1

disc = be*be - 4.0*al*(ga-h);

    if disc >= 0.0

        c = 0.5*(-be - sqrt(disc))/al;

        if ((c > c_der) | (c < c_izq))

            c = 0.5*(-be + sqrt(disc))/al;

        if ((c > c_der) | (c < c_izq))
Appendix 5: (Continued)

opción = 0;

end

end

end

else opción = 0;

end

if opción == 1

%dir1 = psi_o;

%dir2 = x0;

%dir3 = xc;

permiso = 0;

[psi_o,x0,xc,x_cen]=sep_placas(psi1,psi2,c,permiso,xd); /* put in last argument because left out*/

%fprintf('dirr.mat: %f %f %f \n', psi_o,x0,xc);

if h > x_cen

if xc > x_cen

x_izq = x_cen;
Appendix 5: (Continued)

c_izq = c_cen;

    x_cen = xc;

    c_cen = c;

else  x_izq = xc;

    c_izq = c;

end

else

    if xc < x_cen

        x_der = x_cen;

        c_der = c_cen;

        x_cen = xc;

        c_cen = c;

    else x_der = xc;

        c_der = c;

    end

end /* End Opcion 1 */

else
Appendix 5: (Continued)

c = c_cen;

xc=x_cen;

if xc > h
    c_der = c;
    x_der = xc;
else c_izq = c;
    x_izq = xc;
end

c_cen = 0.5*(c_der+c_izq);

%dir1 = psi_o;

%dir2 = x0;

%dir3 = x_cen;

permiso = 0;

[psi_o,x0,xc,x_cen]=sep_placas(psi1,psi2,c_cen,permiso,xd); %/*put xd in last argument because left out*/

xc = x_cen;


c = c_cen;
Appendix 5: (Continued)

end

er1 = absval(h-xc);

er2 = absval(c_der-c_izq);

cmin = c;

xmin = xc;

end %/* if */

%end %/* if */

else

c_izq = cmap(1);

c_der = cmax2;

if (er1 > epsilon) & ( er2 > 0.01*epsilon)

c = 0.5*(c_der + c_izq);

xc = sep_mon(psi1,psi2,c,permiso,xd); %/*put in last argument because left out*/

if (xc > h)

  c_izq = c;

else c_der = c;

end
Appendix 5: (Continued)

```matlab
er1 = absval(h-xc);

er2 = absval(c_der-c_izq);

end /* if */

cmax2 = c;

end

permiso = 0;

if caso == 1

pot= RKF_Int(psi1,psi2,psi_o,h,c,permiso);

else pot = RKF_Intmon(psi1,psi2,psi_o,h,c,permiso);

end

ret=pot;

arc2.m (Originally written by E. Marquez (1994), modified by C. O’Brien (2003))

function ret=arc2(r1,r2,h,phi)

%jac=zeros(4,4);

%f=zeros(1,4);

%b=zeros(1,4);

epsi = 1.0e-6;
```
Appendix 5: (Continued)

d = h + r1 + r2;

x1 = r2 + 0.5*h;

y1 = -1.0;

x2 = 0.0;

y2 = r1;

x3 = r2.*cos(phi);

y3 = r2.*sin(phi);

const=0.5*pi+phi;

m = sin(const)./cos(const);

error = 1.0;

jac(2,1)= 0.0;

jac(2,3) = 0.0;

jac(3,2) = 0.0;

jac(3,4) = 0.0;

jac(3,1) = m;

jac(3,3) = -1.0;

if absval(error) > epsi
f1 = (x3-x1).*(x3-x1) - (x2-x1).*(x2-x1)+(y3-y1).*(y3-y1) - (y2-y1).*(y2-y1);

f2 = (d-x2).*(d-x2)+(y2.*y2)-(r1.*r1);

f3 = y3-y1-m.*(x3-x1);

f4 = y2.*(y2-y1)+(x2-x1).*(x2-d);

f(1) = f1;

f(2) = f2;

f(3) = f3;

f(4) = f4;

jac(1,1) = 2.0.*(x2-x3);

jac(1,2) = 2.0.*(x1-x2);

jac(1,3) = 2.0.*(y2-y3);

jac(1,4) = 2.0.*(y1-y2);

jac(2,2) = 2.0.*(x2-d);

jac(2,4) = 2.0.*y2;

jac(4,1) = d-x2;

jac(4,2) = 2.0.*x2-x1-d;

jac(4,3) = -y2;
Appendix 5: (Continued)

jac(4,4) = 2.0.*y2-y1;

[q,r]=qr_fact(4,jac);

%q=ones(4);

for k = 1:4

%{

sum1 = 0.0;

for j = 1:4

sum1 = sum1 + q(j,k).*f(j);

end

b(k) = -sum1;

end %} /* next k */

b=back_sub(4,r,b,f);

%f=f+(f==0)*eps;

fprintf('back_sub output: %e, %e \n',f,z);

x1 = x1 + f(1);

x2 = x2 + f(2);

y1 = y1 + f(3);
Appendix 5: (Continued)

\[ y_2 = y_2 + f(4); \]
\[ \text{error} = \text{vecnorm}(4,f); \]
end %} /* End While */

if (y2 < 0.0)
fpprintf("
''Error in arc2!!: %f\n',y2);
end

r3 = (x3 - x1).*(x3-x1)+(y3-y1).*(y3-y1);
m = (x3 - x2).*(x3-x2)+ (y3-y2).*(y3-y2);
l = (2.0.*r3-m)./(2.0.*r3); /* Cosine Theorem */
l=l+(l==0)*eps;
if (1.0 - abs(l)) < 1.0e-10
l = pi;
else if abs(l) < 1.0e-10
l = 0.5*pi;
else
l = sqrt(1.0-(1.*l))./l;

251
Appendix 5: (Continued)

l = atan(l);
end

if l < 0.0
l = pi+l;
end
end

xx=sqrt(r3).*l;
ret=xx;

back_sub.m (Originally written by E. Marquez (1994), modified by C. O’Brien (2003))

function ret=back_sub(n,u,y,f)

z=zeros(1,4);

MAXIMO=90;

for i = 1:MAXIMO-5;

    index(i) = i;
end

nan_location=find(isnan(u));
u(nan_location)=0.000000;

z(index(n)) = y(index(n))./(u(index(n)).*(index(n)));

%z(index(n))=z(index(n))+(z(index(n))==0)*eps;

for k = (n-1):-1:1

{%

i2 = index(k);

sum = 0.0;

for j=(k+1):n

%

j2 = index(j);

sum = sum + u(i2,j2).*z(j2);

z(i2) = (y(i2)-sum)./u(i2,i2);

%z(i2)=z(i2)+(z(i2)==0)*eps;

end %}

end %} /* next i */

end %} /* next j */}

ret=z;
Appendix 5: (Continued)

cube.m (Originally written by E. Marquez (1994), modified by C. O’Brien (2003))

function ret=cube(z)

    ret = z*z*z;

field_potoc2.m (Originally written by E. Marquez (1994), modified by C. O’Brien (2003))

function[p1,p2]=field_potoc2(r1,r2,psi1,psi2,h,t,cmin,xmin,v1,v2,h1,h2,xd,x_ref,cmap,xmap)

Diam_o=0.01e-6;

Q=1;

Z=20;

e=1.6021917e-19;

boltzmann=1.38044e-23;

epsilon=1.0e-5;

t = 308.0; /*Temperature

%s1=zeros(1,30);

%we1=zeros(1,30);

%cmap=zeros(1,50);

%xmap=zeros(1,50);
Appendix 5: (Continued)

%fprintf('cmap field_potoc2: %e \n', cmap);

%/* Roots for Gaussian Quadrature */

s1(1) = -0.993128599185094924786;

s1(2) = -0.963971927277913791268;

s1(3) = -0.912234428251325905868;

s1(4) = -0.839116971822218823395;

s1(5) = -0.746331906460150792614;

s1(6) = -0.636053680726515025453;

s1(7) = -0.510867001950827098004;

s1(8) = -0.373706088715419560673;

s1(9) = -0.227785851141645078080;

s1(10) = -0.076526521133497333755;

for g = 1:10

    s1(10+g) = -s1(10-g+1);

end %/*symetric about zero*/

% /* Weights for Gaussian Quadrature */

we1(1) = 0.017614007139152118312;
Appendix 5: (Continued)

wel(2) = 0.040601429800386941331;
wel(3) = 0.062672048334109063570;
wel(4) = 0.083276741576704748725;
wel(5) = 0.101930119817240435037;
wel(6) = 0.118194531961518417312;
wel(7) = 0.131688638449176626898;
wel(8) = 0.142096109318382051329;
wel(9) = 0.149172986472603746788;
wel(10) = 0.152753387130725850968;

for g = 1:10
    wel(10+g) = wel(10-g+1); %/*symetric about zero */
end

%%%begin field potoc %%%

%fprintf('h: %e \n',h);

d = h + r1 + r2;

ngp = 20;

jgp = 1;
Appendix 5: (Continued)

%/* calculate values of phimax and thetamax */

thetamax = maxangle(r1,r2,d); %switches between 1.57(90 degrees) and -1.57

%thetamax=1.0;

%fprintf('thetamax: %e 
',thetamax);

phimax = pi - thetamax;

%/* Calculate first integral using Gaussian Quadrature */

%/* Integration cycle */

theta1 = 0.5*thetamax*(s1(1)+1.0);

l = arc1(r1,r2,h,theta1);

%fprintf('l: %e 
',l);

s2n_ = 0.0;

s2np = 0.0;

s1n_ = 0.0;

s1np = 0.0;

%/* Integrate for distances up to 4 with flat_ocfe2 */

cmax2 = 10.0*cosh(psi1);

cmap(1)=cmin;
Appendix 5: (Continued)

\[
x_{\text{map}}(1) = x_{\text{min}};
\]

\[
\text{if} \ (l <= 5.0) \ & \ (\text{jgp} <= \text{ngp})
\]

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Appendix 5: (Continued)

end

jgp=jgp+1;

if jgp <= ngp

%

theta1 = 0.5.*thetamax.*(s1(jgp) + 1.0);

l = arc1(r1,r2,h,theta1);

if (l-h) < 0.0

fprintf(' Error 1 in field_potoc2: arclength2 < 0.0 !!! %f %f %f %f\n',theta1,l,h);

    end

end %}

end %} /* End While 2 */

% /* Integrate for distances > 5.0 with flat_ocfe */

c1 = (log(v1/v2)./(h1-h2));

c1=c1+(c1==0)*eps;

c2 = log(v1)-c1*h1;

if jgp <= ngp

% */ 3 */

259
Appendix 5: (Continued)

tterm1 = flat_hhf(l,t,psi1,psi2); %where problem occurs

term1 = tterm1*\sin(\theta_1)\cdot w1(jgp);

\text{term2} = \exp(c1*l + c2)\cdot \sin(\theta_1)\cdot w1(jgp);

\text{if term1 < 0.0}

\text{s1n} = \text{s1n} + \text{term1} ;

\text{else}

\text{s1np} = \text{s1np} + \text{term1} ;

\text{end}

\text{if term2 < 0.0}

\text{s2n} = \text{s2n} + \text{term2} ;

\text{else}

\text{s2np} = \text{s2np} + \text{term2} ;

\text{end}

\text{jgp} = jgp+1;

\text{if jgp} \leq \text{ngp}

% \{

\theta_1 = 0.5 \cdot \text{thetamax} \cdot (s1(jgp) + 1.0);

\}
Appendix 5: (Continued)

l = arcl(r1,r2,h,theta1); 

    if (l-h) < 0.0

fprintf(' Error 2 in field_protoc: arclength2 < 0.0 !!! \%f \%f \%f \n',theta1,l,h);

    end

end  

end  

end  

end  

*/ End While 3 */

inhhf1 = 0.5*thetamax*(s1n_ + s1np);

intoc1 = 0.5*thetamax*(s2n_ + s2np);

*/ End Integration 1 */

*/ Calculate second integral using Gauss' quadrature */

*/ Integration Cycle */

if (r1 == r2)&(psi1 == psi2)

    
    p1 = (r1+r2)*inhhf1;

    p2 = (r1+r2)*intoc1;

    fprintf('p1,p2 field_protoc2: \%e \%e \n',p1,p2);

    */
Appendix 5: (Continued)

else

{%

  jgp = 1;
  
cmax2 = 10.0*cosh(psi1);
  
cmin = cmap(1);
  
xmin = xmap(1);
  
  phi1 = 0.5*phimax.*(s1(1)+1.0);
  
l = arc2(r1,r2,h,phi1);
  
s2n_  = 0.0;
  
s2np  = 0.0;
  
s1n_  = 0.0;
  
s1np  = 0.0;

if (l <= 5.0) & (jgp <= ngp)

  {/* 2 */

    tterm1 = flat_hhf(l,t,psi1,psi2);
    
    term1=tterm1*sin(phi1)*we1(jgp);
    
    tterm2 = flat_ocfe(l,t,psi1,psi2,x_ref,cmap,cmax2,xd,xmin,cmin,xmap);

262
Appendix 5: (Continued)

```
term2 = term2*sin(phi1)*we1(jgp);

if term1 < 0.0

    s1n_ = s1n_ + term1 ;

else

    s1np = s1np + term1;

end

if term2 < 0.0

    s2n_ = s2n_ + term2 ;

else

    s2np = s2np + term2;

end

jgp = jgp + 1;

if jgp <= ngp

    % {

    phi1 = 0.5*phimax*(s1(jgp) + 1.0);

    l = arc2(r1,r2,h,phi1);

    if (l-h) < 0.0
```
Appendix 5: (Continued)

```plaintext
fprintf(' Error 3 in field_protoc : arclength2 < 0.0 !!! %f %f %f %f %f %f %f %f %f
'n',theta1,phi1,l,h,thetamax,r1,r2);

end

dd %}

end %} /* End While 2 */

/* Integrate for distances > 5.0 with flat_ocfe */

c1 = log(v1/v2)./(h1-h2);

c2 = log(v1)-(c1*h1);

if jgp <= ngp

% { /* 3 */

term1 = flat_hhf(l,t,psi1,psi2);

term1=term1*sin(phil)*we1(jgp);

term2 = exp(c1*l + c2)*sin(phil)*we1(jgp);

if term1 < 0.0

   s1n_ = s1n_ + term1 ;

else s1np = s1np + term1;

end
```

264
Appendix 5: (Continued)

if term2 < 0.0

s2n_ = s2n_ + term2;

else s2np = s2np + term2;

end

jgp = jgp + 1;

if jgp <= ngp

{"%

phi1 = 0.5*phimax*(s1(jgp) + 1.0);

l = arc2(r1,r2,h,phi1);

if (l-h) < 0.0

fprintf(' Error 4 in field_protoc: arclength2 < 0.0 !!! %f %f %f %f %f %f %f %f %f %f %f
\n',theta1,phi1,l,h,thetamax,r1,r2);

end

end %}

end %} /* End While 3 */

%/* End Integration */

inthhf2 = 0.5*phimax*(s1n_ + s1np);
Appendix 5: (Continued)

\[ \text{intoc2} = 0.5 \times \text{phimax} \times (s2n_ + s2np) ; \]

\[ p1 = (0.5 \times (r1+r2) \times (r1 \times \text{inhhf1}/r2 + r2 \times \text{inhhf2}/r1)); \]

\[ p2 = (0.5 \times (r1+r2) \times (r1 \times \text{intoc1}/r2 + r2 \times \text{intoc2}/r1)); \]

\%fprintf('p1,p2 field_potoc2: %e %e \n',p1,p2); \% no zero elements

end

flat_hhf.m (Originally written by E. Marquez (1994), modified by C. O’Brien (2003))

\%file used to calculate flat_hhf

function ret=flat_hhf(z,t,psi1,psi2)

    ys1 = psi1;

    ys2 = psi2;

    \%z = h;

    yp = 0.5.*\(y_1 + y_2\);

    y_ = 0.5.*\(y_1 - y_2\);

    thz_2 = ((1.0 - \exp(-z)))/(1.0 + \exp(-z));

    cthz_2 = ((1.0 + \exp(-z)))/(1.0 - \exp(-z));

    ret = (yp.*yp).*\(1 - thz_2\) - (y_*y_).*\(cthz_2 - 1.0\);
Appendix 5: (Continued)

maxangle.m (Originally written by E. Marquez (1994), modified by C. O’Brien (2003))

function ret=maxangle(r1,r2,d)

x1 = 0.0;

error = 100.0;

epsilon=1.0e-5;  %/* Relative Error

if error > epsilon

alpha = (r2.*x1.*x1)./r1 + (d.*x1) - (r1.*r1);

beta = 1.0-((x1.*x1)./r1./r1);

gamma = (r1.*r1) - (x1.*x1);

f = (alpha.*alpha) - (r2.*r2.*beta.*gamma);

df = 2.0.*alpha.*(((2.0.*r2.*x1)./r1) + d)+2.0.*x1.*r2.*r2.*(beta+gamma./r1./r1);

x1_new = x1-f./df;

if abs(x1_new) > 1.0e-10

error = abs((x1_new - x1)./x1_new);

else error = abs((x1_new - x1));

end

x1 = x1_new;
end %} /* end if */

alpha = x1./r1;

if abs(alpha) < 1.0e-4

    value = 0.5*pi;

else

    sss = 1.0 - (power(2,alpha));

    ttt = sqrt(sss)/alpha;

    value = atan(ttt);

end

ret = value;

peclet.m (Originally written by C. O’Brien (2003))

function ret = pecet(D,T,vis,G)

%calculate peclet number

%G = average shear rate

%vis = viscosity of medium

%define constants

kb = 1.38066E-23; %J/K

268
Appendix 5: (Continued)

ret=(3*pi*G*vis*D^3)/(T*kb)

power.m (Originally written by E. Marquez (1994), modified by C. O’Brien (2003))

function ret=power(n,z)

if n == 0
    value = 1.0;
else value = 1.0;
    for i = 1:n
        value = value * z;
    end
end

ret=value;

qr_fact.m

function [q,r]=qr_fact(n,jac)

%t=zeros(4,4);
%p=zeros(4,4);

h=zeros(4,4);

for i = 1:n
for j = 1:n
    if i==j
        p(i,j) = 1.0;
    else
        p(i,j) = 0.0;
    end
    t(i,j) = jac(i,j);
    q(i,j) = 0.0;
    r(i,j) = 0.0;
end

end

i = 0;

for m = 1:(n-1)
    for j=1:n
        z(j) = t(j,m);
    end
    s = 0.0;
    for j = m:n
        %
    end

end
Appendix 5: (Continued)

\[ s = s + z(j)^*z(j); \]

end

\[ s = \sqrt{s}; \]

if \( s > 0.0 \)

\%{Column Structure Check */

\[ i = i + 1; \]

\[ \text{den} = -s*(s+\text{abs}(z(i))); \]

\[ \text{den} = \text{den} + (\text{den} == 0)*\text{eps}; \]

for \( j = 1:(i-1) \)

\[ z(j) = 0.0; \]

end

if \( z(i) > 0.0 \)

\[ z(i) = z(i) + s; \]

else

\[ z(i) = z(i) - s; \]

end

for \( j = 1:n \)
for k = 1:n

    h(j,k) = (z(j)*z(k))./den;

end

for j=1:n

    h(j,j) = h(j,j)+1.0;

end

end

for j = 1:n

for k = m:n

    sum1 = 0.0;

    for l=1:n

        sum1 = sum1 + h(j,l)*t(l,k);

    end

    r(j,k) = sum1;

    r(j,k)=r(j,k)+(r(j,k)==0)*eps;

end */ next k */

end
Appendix 5: (Continued)

for j=1:n

    for k=1:n

        "%{"

        sum2 = 0.0;

        for l=1:n

            sum2 = sum2 + p(j,l)*h(l,k);

        end

        q(j,k) = sum2;

        "}% /* next j */

    end

end

for j=1:n

    for k=1:n

        p(j,k) = q(j,k);

        t(j,k) = r(j,k);

    end

end

"}% /* End column structure check */
Appendix 5: (Continued)

%save qrfact q r;

end %}/* next m */

RKF_Int.m (Originally written by E. Marquez (1994), modified by C. O’Brien (2003))

function ret=RKF_Int(psi1, psi2, psi_o, xd, c, permiso)

hmin=1.0e-9;  %* Min integ. length for forces in stab.

epsilon=1.0e-5;  %/ * Relative Error

a4 = 0.2;

g = 1.0; g = g/135.0;

b1 = 16.0*g;

g = 1.0; g = g/12825.0;

b2 = 6656.0*g;

g = 1.0; g = g/56430.0;

b3 = 28561.0*g;

g = 1.0; g = g/50.0;

b4 = 9.0*g;

g = 1.0; g = g/55.0;

b5 = 2.0*g;
Appendix 5: (Continued)

c_31 = 3.0*g;

g = 1.0; g = g/32.0;

c_32 = 3.0*g; c_33 = 9.0 *g;

g = 1.0; g = g/13.0;

c_41 = 12.0*g;

g = 1.0; g = g/2197.0;

c_42 = 1932.0*g; c_43 = 7200.0*g;

c_44 = 7296.0*g;

g = 1.0; g = g/216.0;

a1 = 25.0*g;

c_51 = 439.0*g;

g = 1.0; g = g/513.0;

c_52 = 3680.0*g;

g = 1.0; g = g/4104.0;

a3 = 2197.0*g;

c_53 = 845.0*g;

c_63 = 1859.0*g;
Appendix 5: (Continued)

\[ g = 1.0; \ g = g/27.0; \]
\[ c_61 = 8.0*g; \]
\[ g = 1.0; \ g = g/2565.0; \]
\[ a2 = 1408.0*g; \]
\[ c_62 = 3544.0*g; \]
\[ g = 1.0; \ g = g/40.0; \]
\[ c_64 = 11.0*g; \]
\[ hmax = 1.0e-4; \]
\[ h = hmax; \]
\[ u2 = psi1; \]
\[ psi = psi1; \]
\[ x = 0.0; \]
\[ sum = 0.0; \]
\[ valido = 1; \]
\[ i = 2; \]
\[ term1 = 0.5*cosh(psi1); \]
\[ termp1 = sinh(psi1)*f(x,psi1,c)/10.0; \]
Appendix 5: (Continued)

termp1 = (cosh(psi1)*sqr(f(x,psi1,c))+sqr(sinh(psi1)))/120.0;

valido = 1;

if (permiso == 1 )

printf('Error 1 in RKF_Int: %9.6f %10.8f %10.8f\n',x,psi,f(x,psi,c));

end

if (abs(psi-psi2) >= epsilon) & (valido ==1)

if psi > psi2

/* 1 */

k1 = h*f(x,psi,c);

xo = x + 0.25*h;

u = psi + 0.25*k1;

if u > psi2

/* 2 */

k2 = h*f(xo,u,c);

xo = x + c_31*h;

u = psi + c_32*k1 + c_33*k2;

if u>psi2

277
Appendix 5: (Continued)

% { /* 3 */

   k3 = h*f(xo,u,c);

   xo = x + c_41*h;

   u = psi + c_42*k1 - c_43*k2 + c_44*k3;

if u > psi2

% { /* 4 */

   k4 = h*f(xo,u,c);

   xo = x + h;

   u = psi + c_51*k1 - 8.0*k2 + c_52*k3 - c_53*k4;

if u > psi2

% { /* 5 */

   k5 = h*f(xo,u,c);

   xo = x + 0.5*h;

   u = psi - c_61*k1 + 2.0*k2 - c_62*k3 + c_63*k4 - c_64*k5;

if u > psi2

% { /* 6 */

   k6 = h*f(xo,u,c);
Appendix 5: (Continued)

\[ r = \text{abs}(k1/360.0 - 128.0*k3/4275.0 - 2197.0*k4/75240.0 + k5/50.0 + 2.0*k6/55.0); \]

\[ \text{if } r < \text{epsilon}/514.19 \]

\[ \text{er}_\text{in} = 4.5; \]

\[ \text{else er}_\text{in} = 0.84*\text{sqrt}(\text{sqrt((epsilon/r))}); \]

\[ \text{end} \]

\[ \text{if } r < \text{epsilon} \]

\[ u1 = \psi + a1*k1 + a2*k3 + a3*k4 - a4*k5; \]

\[ \text{if control}(u1,c)==1 \]

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Appendix 5: (Continued)

sum = sum + h*h*h*(termpp1 + termpp2);

term1 = term2;

termp1 = termp2;

termppl = termpp2;

if (permiso == 1 )

fprintf('Error in RKF_Int: %9.6f %10.8f %10.8f n',x,psi,f(x,psi,c));

end

deedd %}/* 7 */

else h = h*0.1;

end %} 

if er_in < 0.1

h = h*0.1;

else if er_in > 4.0

h = h*4.0;

else h = h*er_in;

end

if h < hmin
Appendix 5: (Continued)

fprintf('Error in RKF_Int: h < hmin.!!!\n');

valido = 0;

end

end %} /* 6 */

else h = h*0.1;
end %} /* 5 */

else h = h*0.1;
end %} /* 4 */

else h = h*0.1;
end %} /* 3 */

else h = h*0.1;
end %} /* 2 */

else h = h*0.1;
end %} /* 1 */

else h = h*0.1;
end

if h > hmax
Appendix 5: (Continued)

h = hmax;

    end

end %} /* End While */

suml = sum;

sum = 0.0;

if (permiso == 1 )

    fprintf('Error in RKF_Int: %9.6f %10.8f %10.8f\n',x,psi,f(x,psi,c));

    end

if (absval(u2) >= epsilon) & (valido == 1) 

    if (control(psi,c) ==1) 

        %} /* 1 */

        k1 = h*f(x,psi,c);

        xo = x + 0.25*h;

        u = psi + 0.25*k1;

        if control(u,c) ==1 

            %} /* 2 */

            k2 = h*f(xo,u,c);
Appendix 5: (Continued)

\[ \text{x}_0 = x + c_{31}h; \]

\[ u = \psi + c_{32}k_1 + c_{33}k_2; \]

if control(u,c) == 1

\% \{ /* 3 */

\[ k_3 = h \times f(x_0,u,c); \]

\[ x_0 = x + c_{41}h; \]

\[ u = \psi + c_{42}k_1 - c_{43}k_2 + c_{44}k_3; \]

if control(u,c)==1

\% \{ /* 4 */

\[ k_4 = h \times f(x_0,u,c); \]

\[ x_0 = x + h; \]

\[ u = \psi + c_{51}k_1 - 8.0k_2 + c_{52}k_3 - c_{53}k_4; \]

if control(u,c)==1

\% \{ /* 5 */

\[ k_5 = h \times f(x_0,u,c); \]

\[ x_0 = x + 0.5h; \]

\[ u = \psi - c_{61}k_1 + 2.0k_2 - c_{62}k_3 + c_{63}k_4 - c_{64}k_5; \]
Appendix 5: (Continued)

if control(u,c)==1

  %{ /* 6 */

    k6 = h*f(xo,u,c);

    r = absval(k1/360.0 - 128.0*k3/4275.0 - 2197.0*k4/75240.0 + k5/50.0 + 2.0*k6/55.0);

    if r < (epsilon/514.19)

      er_in = 4.5;

    else er_in = 0.84*sqrt(sqrt((epsilon/r)));

  end

  if r < epsilon

    %{

      u1 = psi + a1*k1 + a2*k3 + a3*k4 - a4*k5;

      if control(u1,c)==1

        %{ /* 7 */

          psi = u1;

          x = x+h;

          u2 = f(x,psi,c);

          term2 = 0.5*cosh(psi);

  284
Appendix 5: (Continued)

termp2 = sinh(psi)*u2/10.0;

termpp2 = (cosh(psi)*u2*u2+sqr(sinh(psi)))/120.0;

sum = sum+h*(term1 + term2);

sum = sum+h*h*(termp1 - termp2);

sum = sum+h*h*h*(termpp1 + termpp2);

term1 = term2;

termp1 = termp2;

termpp1 = termpp2;

if (permiso == 1)

fprintf('Error in RKF_Int: %9.6f %10.8f %10.8f %10.8f %10.8f %10f\n','x,psi,u2,er_in,r,h);

end

end */ 7 */

else h = h*0.1;

end %}

if er_in < 0.1

h = h*0.1;
Appendix 5: (Continued)

else if er_in > 4.0

    h = h*4.0;

else h = h*er_in;

end

if h < hmin

    fprintf('Error in RKF_Int: h < hmin.!!!!\n');

    valido = 0;

end

end %} /* 6 */

else h = h*0.1;

end %} /* 5 */

else h = h*0.1;

end %} /* 4 */

else h = h*0.1;

end %} /* 3 */

else h = h*0.1;

end %} /* 2 */
Appendix 5: (Continued)

else h = h*0.1;

   end %} /* 1 */

else h = h*0.1;

end

   if h > hmax

       h = hmax;

   end

   end %} %/* End While */

sum = 2.0*sum + sum1;

sum = -2.0*sum + xd*(cosh(psi_o)+1.0)+ 4.0*(cosh(0.5*psi1)+cosh(psi2*0.5)-2.0);

ret=sum;

RKF_Intmon.m (Originally written by E. Marquez (1994), modified by C. O’Brien (2003))

function ret=RKF_Intmon(psi1, psi2, psi_o, xd, c, permiso)

hmin=1.0e-9;  %* Min integ. length for forces in stab.

hmax = 1.0e-4;

h = hmax;

287
Appendix 5: (Continued)

u2 = psi1;

psi = psi1;

x = 0.0;

sum = 0.0;

i = 2;

epsilon=1.0e-5;  /* Relative Error */

a4 = 0.2;

    g = 1.0; g = g/135.0;

    b1 = 16.0*g;

    g = 1.0; g = g/12825.0;

    b2 = 6656.0*g;

    g = 1.0; g = g/56430.0;

    b3 = 28561.0*g;

    g = 1.0; g = g/50.0;

    b4 = 9.0*g;

    g = 1.0; g = g/55.0;

    b5 = 2.0*g;
c_31 = 3.0*g;

g = 1.0; g = g/32.0;

c_32 = 3.0*g; c_33 = 9.0 *g;

g = 1.0; g = g/13.0;

c_41 = 12.0*g;

g = 1.0; g = g/2197.0;

c_42 = 1932.0*g; c_43 = 7200.0*g;

c_44 = 7296.0*g;

g = 1.0; g = g/216.0;

a1 = 25.0*g;

c_51 = 439.0*g;

g = 1.0; g = g/513.0;

c_52 = 3680.0*g;

g = 1.0; g = g/4104.0;

a3 = 2197.0*g;

c_53 = 845.0*g;

c_63 = 1859.0*g;
Appendix 5: (Continued)

g = 1.0; g = g/27.0;

c_61 = 8.0*g;

g = 1.0; g = g/2565.0;

a2 = 1408.0*g;

c_62 = 3544.0*g;

g = 1.0; g = g/40.0;

c_64 = 11.0*g;

term1 = 0.5*cosh(psi1);

termp1 = sinh(psi1)*f(x,psi1,c)/12.0;

termppl = ( cosh(psi1)*sqr(f(x,psi1,c))+sqr(sinh(psi1)))/120.0;

valido = 1;

if permiso == 1

fprintf('Error in RKF_Intmon: %9.6f %10.8f %10.8f\n',x,psi,f(x,psi,c));

end

if absval(psi-psi2) >= epsilon & (valido ==1)

%

if psi > psi2

290
Appendix 5: (Continued)

\%{ /* 1 */

k1 = h*f(x,psi,c);

xo = x + 0.25*h;

u = psi + 0.25*k1;

if u > psi2

\%{ /* 2 */

k2 = h*f(xo,u,c);

xo = x + c_31*h;

u = psi + c_32*k1 + c_33*k2;

if u > psi2

\%{ /* 3 */

k3 = h*f(xo,u,c);

xo = x + c_41*h;

u = psi + c_42*k1 - c_43*k2 + c_44*k3;

if u > psi2

\%{ /* 4 */

k4 = h*f(xo,u,c);
Appendix 5: (Continued)

\[ xo = x + h; \]

\[ u = psi + c_{51} \cdot k1 - 8.0 \cdot k2 + c_{52} \cdot k3 - c_{53} \cdot k4; \]

if \( u > psi2 \)

% \{ /* 5 */ \}

\[ k5 = h \cdot f(xo,u,c); \]

\[ xo = x + 0.5 \cdot h; \]

\[ u = psi - c_{61} \cdot k1 + 2.0 \cdot k2 - c_{62} \cdot k3 + c_{63} \cdot k4 - c_{64} \cdot k5; \]

if \( u > psi2 \)

% \{ /* 6 */ \}

\[ k6 = h \cdot f(xo,u,c); \]

\[ r = \text{absval}(k1/360.0 - 128.0 \cdot k3/4275.0 - 2197.0 \cdot k4/75240.0 + k5/50.0 + 2.0 \cdot k6/55.0); \]

if \( r < \text{epsilon}/514.19 \)

\[ \text{er}_\text{in} = 4.5; \]

else \( \text{er}_\text{in} = 0.84 \cdot \sqrt{\sqrt{(\text{epsilon}/r))}}; \)

end

if \( r < \text{epsilon} \)

% \{
u1 = psi + a1*k1 + a2*k3 + a3*k4 - a4*k5;

if control(u1,c)==1

%' /* 7 */

psi = u1;

x = x+h;

u2 = f(x,psi,c);

term2 = 0.5*cosh(psi);

termp2 = sinh(psi)*u2/10.0;

termpp2 = (cosh(psi)*u2*u2+sqr(sinh(psi)))/120.0;

sum = sum + h*(term1 + term2);

sum = sum + h*h*(termp1 - termp2);

sum = sum + h*h*h*(termpp1 + termpp2);

term1 = term2;

termp1 = termp2;

termpp1 = termpp2;

if (permiso == 1)
Appendix 5: (Continued)

fprintf('Error in RKF_Intmon: %9.6f %10.8f %10.8f %10.8f %10.8f %10f\n',x,psi,u2,er_in,r,h);

end

end %} /* 7 */

else h = h * 0.1;

end %} )

if er_in < 0.1

h = h * 0.1;

else if er_in > 4.0

h = h * 4.0;

else h = h * er_in;

end

if h < hmin

fprintf('Error in RKF_Intmon: h < hmin.!!!\n');

valido = 0;

end

end %} /* 6 */
Appendix 5: (Continued)

else

    h = h * 0.1;

end /* 5 */

else h = h * 0.1;

end /* 4 */

else h = h * 0.1;

end /* 3 */

else h = h * 0.1;

end /* 2 */

else h = h * 0.1;

end /* 1 */

else h = h * 0.1;

end

if h > hmax

    h = hmax;

end

end /* End While */

295
Appendix 5: (Continued)

\[ a_{n1} = 0.5 \psi_1; \ a_{n2} = \psi_2 \times 0.5; \]

\[ \text{sum} = -2.0 \times \text{sum} + x_d \times (1.0 - 0.5 \times c) + 4.0 \times (\cosh(a_{n1}) + \cosh(a_{n2}) - 2.0); \]

\[ \text{ret} = \text{sum}; \]

vecnorm.m (Originally written by E. Marquez (1994), modified by C. O’Brien (2003))

function \( \text{ret} = \text{vecnorm}(n,z) \)

\[ \text{norm} = \text{absval}(z(1)); \]

for \( i = 2:n \)

\[ \text{if absval}(z(i)) > \text{norm} \]

\[ \text{norm} = \text{absval}(z(i)); \]

end

end

\[ \text{ret} = \text{norm}; \]

eucnorm.m (Originally written by E. Marquez (1994), modified by C. O’Brien (2003))

function \( \text{ret} = \text{eucnorm}(n,z) \)

\[ \text{norm} = z(1) \times z(1); \]

for \( i = 2:n \)

\[ \text{norm} = \text{norm} + z(i) \times z(i); \]
Appendix 5: (Continued)

end

ret=norm;