AGGREGATION OF POLYMER PARTICLES IN EMULSION

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZURICH (ETHZ)
for the degree of
Doctor of Technical Sciences

Presented by

Marinus Aris Verduyn

M.Sc. Delft University of Technology
born September 15, 1971
Citizen of the Netherlands

accepted on the recommendation of

Prof. Dr. M. Morbidelli, examiner
Prof. Dr. J. Baldyga, co-examiner
Dr. G. Storti, co-examiner

Zurich 1999
Science is not and never will be a closed book.
Every important advance brings new questions.
Every development reveals, in the long run, new and deeper difficulties ...

(Albert Einstein and Leopold Infeld)
Acknowledgements

Words alone are of course only a limited way of expressing my thanks to all who contributed to the completion of my Ph.D.-project. However, let me attempt to do so:

- Prof. Massimo Morbidelli, for the great management of my Ph.D.-project and enabling me to do this in his group

- Prof. Jerzy Baldyga, for the valuable cooperation, constructive criticism, and coagulation modeling initiatives during all stages from start to finish of my Ph.D.-project

- Dr. Giuseppe Storti, for the extensive input on the colloidal area and concerning PBE-modeling, his 'helicopter view' as well as maintaining the link between experimental and modeling activities

- Dr. Stefano Melis, for the cooperation on several topics within our subgroup on coagulation

- Prof. Konrad Hungerbühler, for welcoming me as a Ph.D.-student at ETH and facilitating the transition to my ultimate group

- Franz Mayer, for the analytical support particularly with the ion chromatography and the organization of numerous 'Apéros' in his lab

- Prof. Peter Schurtenberger, for introducing us to light-scattering techniques and letting me use the equipment of his group for the very first coagulation experiments

- Prof. Sangtae Kim, for his help with the computation of the mobility functions

- Dr. Oeemer Kut, who always behaved like 'il postino'

- Claire Mills, for struggling through my thesis and making valuable improvements in the spelling and the grammar

- My parents, for their care and support, although they were most of the time in the Netherlands, I always had the feeling that they were close to me

- Marcelina, for her love and support, I am looking forward to the continuation of our fantastic relationship

as well as my colleague Ph.D.-students and other (former) members of our group like the second Polish contingent Adam Kisielewski, and all other persons I did not mention here.
# Contents

1 Introduction  
1.1 Generalities on emulsion polymerization  4

2 Population balance equations  7

3 Governing equations describing relative particle motion and aggregation  15  
3.1 Relative particle motion due to the fluid velocity field  18  
3.2 Brownian diffusion  22  
3.3 Colloidal interaction  23  
  3.3.1 The attractive potential energy of interaction  24  
  3.3.2 The repulsive potential energy of interaction  25  
3.4 The complete convection-diffusion equation  29  
3.5 Dimensionless representation  33  
  3.5.1 Perikinetic coagulation  34  
  3.5.2 Orthokinetic coagulation  35  
  3.5.3 Peri- and orthokinetic coagulation  38  
3.6 Two-dimensional model for arbitrary Péclet numbers  41  
3.7 Results obtained with the two-dimensional model  42

4 Development of simplified models for aggregation  53  
4.1 Turbulent diffusion model  54  
4.2 Convective motion model employing two zones  59  
  4.2.1 Characteristics derived from the convective motion model  67  
  4.2.2 Comparison for unequal-sized particles  67

5 Experimental validation of the model  69  
5.1 Introduction  69  
5.2 Experimental procedure  69
5.2.1 Preparation of polystyrene latex dispersions ............... 69
5.2.2 Perikinetie coagulation experiments ...................... 71
5.2.3 Sampling and characterization ............................ 73
5.3 Techniques used for characterization ........................ 74
  5.3.1 Gravimetry ........................................... 74
  5.3.2 Dynamic light-scattering (DLS) .......................... 75
  5.3.3 Scanning electron microscopy (SEM) ...................... 78
  5.3.4 Zeta potential ......................................... 80
  5.3.5 Adsorption of surfactant ............................... 81
  5.3.6 Ion chromatography ................................... 86
  5.3.7 Ultrafiltration .......................................... 87
  5.3.8 Soap titration .......................................... 88
5.4 Population balance equation model ........................... 89
  5.4.1 Numerical solution of the population balance equations .... 90
5.5 Comparison between experimental results and predictions from the PBE ... 92
5.6 Discussion on counterion adsorption isotherm ............... 104
  5.6.1 Zeta potential measurements at various NaCl concentrations ... 106
  5.6.2 An empirical model for the counterion adsorptivity .......... 110
5.7 Sensitivity study for the stability ratio W ........................ 114

6 Conclusions .................................................. 117

A Hydrodynamic interaction functions for diffusion .............. 119

B Hydrodynamic interaction functions for convective motion ...... 123

C Behaviour of the ratio $\frac{1 - A}{C}$ ........................................ 133
Abstract

A comprehensive model for particle coagulation in polymeric latices subject to turbulent flow was developed. It is based on the convection-diffusion equation for a single pair of particles embedded in an extensional flow field. Also for the other two particle transport mechanisms, Brownian diffusion and particle motion induced by colloidal particle interaction, the hydrodynamic interaction between the two particles is properly taken into account. Simulations using the convection-diffusion equation show that the rate of coagulation is sensitive to fluid motion mainly for colloidal systems where the electrical double layer is thick. Although larger particle sizes are collooidally more stable, the aggregation rate may increase with particle size when the double layer is thick and the flow field sufficiently intense.

Two simplified coagulation models were developed involving only ordinary differential equations but still taking into account all particle transport mechanisms. There is good agreement with the predictions obtained from the detailed model when the extensional flow field is split into two regions. The second simplified model uses gradient diffusion as closure for the turbulent particle transport term, but this is shown to work properly only for colloidal unstable systems.

The time evolution of the particle size distribution is predicted with the help of a population balance equation which, due to the underlying particle coagulation model, can be employed mainly for the stage where doublet formation dominates. To validate the model predictions, perikinetic coagulation experiments with well-characterized polystyrene latex dispersions were carried out. Different values of emulsifier surface coverage and particle size were examined at different salt concentrations. To predict the zeta potential, an empirical model for the adsorption of counterions in the Stern layer was formulated, and the model parameters were identified by comparison between the experimentally measured evolution of the average particle size and the predicted one. The predicted time evolution of the whole particle size distribution demonstrates the possible formation of a multimodal particle size distribution during coagulation.
Zusammenfassung

Ein umfassendes Modell für die Koagulation von Teilchen in Polymerdispersionen mit turbulenter Strömung wurde aufgestellt. Das Modell basiert auf der Konvektions-Diffusionsgleichung für ein einzelnes Teilchenpaar in einem sich ausdehndenden Strömungsfeld. Auch für die übrigen zwei Teilchentransportmechanismen, Brownsche Diffusion und durch kolloidale Wechselwirkung induzierte Teilchenbewegung, wurde die hydrodynamische Wechselwirkung korrekt berücksichtigt. Simulationen auf der Basis der Konvektions-Diffusionsgleichung zeigen, dass die Koagulationsgeschwindigkeit vorwiegend für den Fall kolloidaler Systeme mit dicken elektrischen Doppelschichten von der Flüssigkeitsströmung beeinflusst wird. Obwohl grössere Teilchen kolloidal stabiler sind, kann die Koagulationsgeschwindigkeit bei grösseren Teilchengrössen zunehmen, wenn die Doppelschicht relativ dick und das Strömungsfeld genügend stark ist.

Zwei vereinfachte Modelle für die Teilchenkoagulation, die nur gewöhnliche Differentialgleichungen enthalten, aber trotzdem alle Teilchentransportmechanismen berücksichtigen, wurden entwickelt. Deren Voraussagen sind in guter Übereinstimmung mit jenen des detaillierten Modells, wenn das sich ausdehnde Strömungsfeld in zwei Regionen aufgespalten wird. Das zweite vereinfachte Modell verwendet "gradient diffusion" als Schliessterm des turbulenten Teilchentransportterms, seine Anwendbarkeit ist aber auf kolloidal instabile Systeme beschränkt.

Chapter 1

Introduction

For the industrial production of polymers such as polystyrene, polyvinylacetate, and many others, emulsion polymerization is often used. Approximately 15% of the Western world’s 10^8 tons/year of polymers is produced by emulsion polymerization processes (Gilbert, 1995). Such polymers find application in a large variety of products such as latex paints, rubbers, coatings, and adhesives. Usually the polymer is obtained as an aqueous dispersion of very small colloidal particles, the so-called latex. Important characteristics of the latex product are its chemical composition and molecular weight distribution but in particular its particle size distribution. This affects not only the colloidal stability of the emulsion during production but, in the case of polymers whose final application is in the form of latices, it defines also applicative properties such as rheological behaviour and adhesion characteristics, and therefore the commercial value of the final product.

In short, emulsion polymerization is a free radical polymerization performed in a heterogeneous reaction system, usually a stirred tank reactor, yielding submicron solid polymer particles dispersed in an aqueous medium. Initially, the reaction mixture consists of water containing dispersed monomer droplets. A characteristic feature of many emulsion polymerization processes is the application of surfactants. The surfactants are used to provide colloidal stability for both the monomer droplets and the polymer particles.

The evolution of the particle size distribution during emulsion polymerization is affected by particle nucleation, particle growth due to addition of monomer units and aggregation of particles. The aim of this study is to deepen our current understanding of particle coagulation in polymeric latices, accounting for the three particle transport mechanisms which simultaneously play a role during coagulation. These are Brownian diffusion and particle motion induced by colloidal particle interaction and (turbulent) fluid motion.
In the literature so far, so-called perikinetic coagulation, where Brownian diffusion and colloidal interactions are taken into account, has been studied intensively. Since the first publications on perikinetic coagulation (Fuchs, 1936; Derjaguin and Muller, 1967), the weak point has been the description of the colloidal interaction part, for which traditionally DLVO theory has been used (see for instance Verwey and Overbeek, 1948). Several parameters of difficult evaluation are involved (such as the zeta potential) and they all have a strong influence on the calculated rate of aggregation. Notably, most of the recent literature works focused on coagulation in the perikinetic regime are based on DLVO, although some areas of this theory concerning the electrostatic interaction should be investigated further.

On the other hand, so-called orthokinetic coagulation where only fluid motion is active as a particle transport mechanism, was discussed first by Smoluchowski (1917) for a simple shear flow and has received considerable attention afterwards (van de Ven and Mason, 1976; Adler, 1981a,b). However, although considerable attention was paid to orthokinetic coagulation in a turbulent flow field (Camp and Stein, 1943; Saffman and Turner, 1956) only few considered an extensional flow (Pnueli et al., 1991; Adler, 1981a), which is most suitable for the description of the microflow on the scale of the coagulating particles.

Finally, in the literature so far there have been only few publications in which all transport mechanisms were accounted for at the same time (Zinchenko and Davis, 1994a,b); the remaining publications considered either perikinetic coagulation with a small orthokinetic contribution (van de Ven and Mason, 1977b), or orthokinetic coagulation with a small perikinetic contribution (Zeichner and Schowalter, 1977; van de Ven and Mason, 1977a). Following Levich (1962), Gruy and Saint-Raymond (1997) proposed a model employing turbulent diffusion, but this model appeared to be incorrect as discussed later in section 4.1 of this thesis. Swift and Friedlander (1964) adopted an oversimplified approach by using the sum of the peri- and orthokinetic coagulation rates but this approach cannot be generalized and is allowed only for unstable cases as we demonstrated by numerically solving the convection-diffusion equation (Melis et al., 1999).

The approach adopted in this study to build a comprehensive model for particle coagulation is rather fundamental, so as to be applied to different conditions, monomer species and reactor types (batch and semibatch). However, the final result is intended to provide practical indications on how to operate the reactor and which variables to manipulate (e.g. stirring rate, reactor geometry, initial amounts and feeding rates of surfactants, initiators and monomers, solution pH) to obtain at the end of the process the desired particle size.
distribution. It is worth mentioning that although the results of this study are aimed at polymerization in emulsion, they can also be applied to other heterogeneous processes such as crystallization, precipitation and coalescence of bubbles and droplets for instance in atmospheric phenomena.

This thesis is organized as follows:

In chapter 2 the key modeling tool for the description of the time evolution of particulate systems, the population balance equation, is described. After a comprehensive discussion, the population balance suitable for the particular system under examination is obtained. Following this, a fundamental "local" approach is presented aimed at the microscopic description of the behaviour of a pair of interacting particles embedded in a defined flow field. This coagulation model is based on the so-called convection-diffusion equation and all different particle transport mechanisms which affect particle coagulation (Brownian diffusion, colloidal interaction and fluid motion) are accounted for. Each transport mechanism is separately discussed and evaluated through sets of equations or submodels.

On the topic of the flow field, the structure at the scale of the coagulating particles depends on the flow regime in the reactor, laminar or turbulent. We consider a turbulent flow field and employ an extensional flow field on the scale of the coagulating particles. Special attention is drawn to the disturbance of the relative particle motion by fluid squeezing when two particles come into each others neighbourhood.

The colloidal interaction is described in terms of DLVO theory and we distinguish an attractive and a repulsive contribution. In particular the electrostatic repulsion requires special attention since it determines the location and the value of the potential energy barrier which needs to be overcome for coagulation to occur. A Stern layer submodel is used to predict the key parameter for colloidal repulsion, the so-called zeta potential. This model takes into account the adsorption of emulsifier on the surface of the particles which is in turn affected by the electrolyte concentration in the continuous phase. Additionally, an adsorption isotherm for specifically adsorbed counterions is proposed.

The solution to the resulting convection-diffusion equation yields the rate of coagulation for a pair of particles. Several kinds of parametric calculations are performed to investigate the sensitivity to fluid motion of latex dispersions with varying electrical double layer thicknesses, the coagulation behaviour of stable and unstable latex dispersions, and the effect of particle size. Moreover, the coagulation behaviour of unequal-sized particles is discussed.
Chapter 4 presents two simplified models which reduce the computational effort to solve the convection-diffusion equation in the previous chapter. The first employs the concept of gradient diffusion as closure for the turbulent transfer term in the convection-diffusion equation. The second (simplified model) is based on division of the extensional flow field around a particle into separate regions. Both simplified models are compared to the results of the convection-diffusion equation and the second one is selected to be used in population balance equations.

The aim of the fifth chapter is to validate the predictions of the population balance equation in the perikinetic limit. Coagulation experiments induced by salt addition are carried out under well-defined conditions and with well-characterized initial polystyrene dispersions, stabilized with an ionic emulsifier (SDS). Spent latex dispersions are used so as to restrict ourselves to the coagulation terms in the population balance equation. The different techniques used to measure the colloidal characteristics of the dispersions are described. The time evolution of the average particle size is monitored by dynamic light-scattering and is compared to the predictions of the population balance equation. Different initial values of emulsifier coverage and particle size are examined at different salt concentrations. Comparison between the measurements and the simulations allows us to obtain a better insight in the counterion adsorption isotherm used in the Stern layer model and formulate an empirical model for the counterion adsorptivity. This provides a rather severe test of the model reliability. Moreover, investigation of the evolution of the particle size distribution obtained from the population balance equation provides qualitative understanding of the dynamics of the different coagulation experiments.

Finally, chapter 6 draws conclusions regarding the overall experimental and modeling activities that were performed in this work. As well, an outlook of future work in this field is briefly given.

1.1 Generalities on emulsion polymerization

Since the focus of this work is to achieve a better understanding of coagulation in emulsion polymerization reactors, let us discuss the main aspects of this polymerization process (Gilbert, 1995).

Emulsion polymerization is a heterogeneous polymerization process where at most three phases are present:

- the aqueous phase which is also the continuous one,
- the monomer phase, dispersed in the aqueous phase in the form of droplets,

- the polymer phase, dispersed in the aqueous phase in the form of a population of monomer-swollen polymer particles.

To keep the monomer droplets and polymer particles dispersed, the emulsion polymerization reactor is equipped with an agitation device, for a stirred tank reactor usually an impeller.

![Conversion vs Time Graph](https://via.placeholder.com/150)

**Figure 1.1:** Schematic representation of the different intervals in ab-initio batch emulsion polymerization of sparsely water-soluble monomers.

During batch emulsion polymerization of sparsely water-soluble monomers such as styrene, three time-separated intervals can be distinguished: see Fig. 1.1: particle formation (I), particle growth with (II), and without (III) monomer droplets present (Smith and Ewart, 1948). At typical emulsifier concentrations particle formation is dominated by micellar nucleation. Once the water soluble initiator is added, thermal decomposition into radicals occurs. The actual polymerization starts in the aqueous phase by reaction of a monomer molecule with an initiator radical. After a few propagation steps in the aqueous phase, the oligomer radical enters a monomer-swollen micelle and a particle is formed. In this freshly formed polymer particle, which then becomes the locus of polymerization, a polymer chain starts growing. At the end of interval I all micelles have disappeared and particle nucleation stops. The surfactant, initially solubilized in the aqueous phase and mostly present as micelles, is continually adsorbed onto the surface of the growing particles to provide colloidal stability. At a certain conversion, the amount of adsorbed emulsifier
is such that no more micelles are present and the first reaction interval ends. During the second stage of the process, the polymerization takes place in the monomer-swollen particles. Since monomer droplets are present as a separate phase, one can assume that the concentration of monomer in the particles remains constant during this reaction interval. At a conversion typically around 30 – 40%, the droplets disappear and the second reaction interval finishes. In the third stage, the reaction rate declines due to a decrease of the monomer concentration in the polymer particles.

Emulsion polymerization has some significant advantages over other industrial polymerization processes such as bulk and solution polymerization:

- It produces polymers of high molecular weight at high polymerization rates. This is possible due to the reduced probability of having termination reactions among growing radicals because they are segregated in the different particles.

- It provides easy temperature control. The polymerization heat is produced in the polymer particles which have a very large surface-to-volume ratio so the heat is rapidly transferred to the continuous aqueous phase from which it is then removed through the cooling elements.

- Emulsion polymerization uses water and no other (e.g. organic) solvents that are expensive and/or hazardous to the environment.

- A number of applications requires the polymer in the form of a latex.
Chapter 2

Population balance equations

In a dispersed phase system the material domain comprises a continuous phase and a dispersed phase, the former being usually represented in physical space by a vector of the local continuous phase variables, which must satisfy the continuum transport equations such as the differential momentum, mass, species and energy balances, and related boundary conditions. The dispersed phase represents a population of particles; the particles are changing with time their spatial positions as well as their properties such as particle size, shape and mass, and chemical composition. The identities of individual particles in the population are being continuously destroyed and recreated by breakup and agglomeration processes. There is a large number of particles in the systems of our interest (such as emulsion polymerization, crystallization, and precipitation), so we would like to consider not properties of the individual particles but instead properties of the population of particles. For this reason the discrete particles in the system are thought of as a continuous distribution; this continuum approach is justified when a large number of particles are contained in any discrete sampling range of the property of interest (Randolph and Larson (1971, 1988)).

In this work we are interested in the a priori prediction of the particle size or mass distribution (our properties of interest); because the kinetics of the particle aggregation, breakup and growth may depend on the position in the physical space, one has to consider in general also spatial distributions of the particle population. Note that from a practical point of view spatial distributions of the particle population can be of high importance showing for example how the concentration of dispersion and related size distribution of particles varies with the sampling position in the tank.

To formulate a mathematical framework for this kind of system, which takes into account our expectations, it is necessary to consider a distribution of particles in both physical space (we refer to the spatial coordinates $\vec{x} = [x_1, x_2, x_3]$ as external coordi-
nates) and "property" space (we refer then to the property coordinates $\vec{s} = [s_1, s_2, \ldots]$ as internal coordinates). The external and internal coordinates form a finite dimensional vector space $\vec{\xi} = [\vec{s}, \vec{s}']$ which is known as a particle state space (Ramkrishna, 1985) or a particle phase space (Randolph and Larson (1971, 1988)). We employ now after Ramkrishna (1985), Randolph and Larson (1971, 1988), and Hulburt and Katz (1964) the concept of a multidimensional particle population distribution $f(\vec{\xi}, t)$ being the average number of particles per unit volume of the particle state space. Hence, $f(\vec{\xi}, t) d\vec{\xi}$ with $d\vec{\xi} = dx_1 dx_2 dx_3 ds_1 ds_2 \ldots$ represents the number of particles in the system with coordinates in the range $\vec{\xi}$ to $\vec{\xi} + d\vec{\xi}$ at time $t$.

Individual particles are continuously changing their position in the particle state space. If these changes are gradual and continuous one can refer (Randolph and Larson (1971, 1988)) to the rate of change of the coordinate of a particle as the convective velocity along coordinate axes. Hence, the rate of change of particle state (particle state velocity) consists of the rate of change of internal coordinates $\frac{d\vec{s}}{dt}$ which is assumed to be a unique function of the state of the particle, and the rate of change of external coordinates $\frac{d\vec{s}'}{dt}$ representing the velocity of the particle through the physical space. The particle velocity is generally not the same as the fluid velocity; consequences of this fact will be discussed in the next chapter. The particle state velocity vector $\vec{u}$ reads then:

$$\vec{u}(\vec{\xi}, t) = \frac{d\vec{\xi}}{dt} = \frac{d\vec{s}}{dt} + \frac{d\vec{\xi}'}{dt}$$ (2.1)

A population balance for particles in some fixed subregion of particle state space leads to the following particle number continuity equation:

$$\frac{\partial f(\vec{\xi}, t)}{\partial t} + \sum_i \frac{\partial [u_i(\vec{\xi}, t) f(\vec{\xi}, t)]}{\partial \xi_i} = h(\vec{\xi}, t)$$ (2.2)

being an analogue to the classical Liouville equation (Hulburt and Katz, 1964). The term $h(\vec{\xi}, t)$ represents the rate of change of the number of particles with phase coordinate $\vec{\xi}$ within the system at time $t$. This is caused by processes such as breakup and coagulation.

For the particle population studies we denote the particle velocity in physical space by $\vec{v} = \frac{d\vec{s}'}{dt}$. When for the internal coordinate $\vec{s}'$ the particle dimension along the $j$-th characteristic axis of the particle is taken, the term $\frac{d\xi_j}{dt}$ equals the growth rate $q_j$. This term is due to processes like chemical reaction and absorption. Hence, for the number density function $f(\vec{s}, \vec{s}', t)$ we obtain:

$$\frac{\partial f(\vec{s}, \vec{s}', t)}{\partial t} + \frac{\partial}{\partial s_j} [g_j(\vec{s}, \vec{s}', t) f(\vec{s}, \vec{s}', t)] + \frac{\partial}{\partial x_i} [v_i(\vec{s}, \vec{s}', t) f(\vec{s}, \vec{s}', t)] = h(\vec{s}, \vec{s}', t)$$ (2.3)
Eqn. 2.3 has been derived assuming that the particles move convectively in the particle state space and that therefore the convective particle population flux $\vec{N}$ takes the form:

$$\vec{N} = \vec{v}(\vec{\xi}, \vec{x}, t)f(\vec{\xi}, \vec{x}, t)$$

(2.4)

where the particle state velocity vector $\vec{v}$ is given by Eqn. 2.1. However, one can also expect diffusive fluxes (Brownian diffusion, random fluctuations in growth rate resulting in growth rate dispersion), so one can represent the particle population flux by a more general equation:

$$\vec{N} = -\overline{D} \cdot \nabla f(\vec{\xi}, \vec{x}, t) + \vec{v}(\vec{\xi}, \vec{x}, t)f(\vec{\xi}, \vec{x}, t)$$

(2.5)

where $\overline{D}$ is a generalized diffusion tensor of particles within the particle state space. For the application in this work the growth rate dispersion is negligible and Brownian diffusion effects will be absorbed into the aggregation kernels; we will in this chapter, however, discuss briefly diffusion effects generated by random fluctuations resulting from turbulent flow.

To formulate the expression for $h(\vec{\xi}, \vec{x}, t)$ on the right-hand side of Eqn. 2.3 in studies of the polymer particle population it is most convenient to choose particle mass $m$ as the internal coordinate. Consequently $f(m, \vec{x}, t)dm$ is the number of polymer particles in the particle mass range from $m$ to $m + dm$ at position $\vec{x}$ in the system at time $t$. Examples of mono- and bimodal particle size (or mass, see Eqn. 2.14 later-on) distributions are given in Fig. 2.1.

Figure 2.1: Examples of mono- (-) and bimodal (o) number density functions $f(v)$. Notice that the relation between particle volume and size is $v = \frac{4}{3}\pi r^3$ for spherical particles.
Including terms for particle coagulation, breakup and nucleation (Kumar and Ramkrishna, 1996) for the term $h(m, \vec{x}, t)$ yields the following population balance equation (PBE) for $f(m, \vec{x}, t)$ which is generally valid:

$$
\frac{\partial f(m, \vec{x}, t)}{\partial t} + \frac{\partial}{\partial m} [g_m(m, \vec{x}, t)f(m, \vec{x}, t)] + \frac{\partial}{\partial x_i} [v_i(m, \vec{x}, t)f(m, \vec{x}, t)] = \\
\left(\frac{1}{2}\right) \int_{m_0}^{m} \beta(m - m', m', \vec{x}, t)f(m - m', \vec{x}, t)f(m', \vec{x}, t)dm' \\
- f(m, \vec{x}, t) \int_{m_0}^{\infty} \beta(m, m', \vec{x}, t)f(m', \vec{x}, t)dm' - \Gamma(m, \vec{x}, t)f(m, \vec{x}, t) \\
+ \int_{m_0}^{\infty} \gamma(m', \vec{x}, t)f(m', \vec{x}, t)dm' + r_m(\vec{x}, t)\delta(m - m_0)
$$

$g_m$ is the rate of increase of particle mass for instance due to chemical reaction (radical polymerization) or absorption of monomer (swelling with monomer).

The first two integral terms on the right-hand side are the birth and death contributions due to particle coagulation. $\beta(m - m', m', \vec{x}, t)$ is the aggregation frequency of two particles having mass $m - m'$ and $m'$, respectively (yielding a new particle of mass $m$). Except for dense suspensions, simultaneous encounters between three or more particles can be ignored (Kusters et al., 1997). Since only binary particle encounters are accounted for, $\beta(m, m', \vec{x}, t)$ can be considered as a second-order kinetic rate constant. In addition to coagulation, the particles can undergo breakup with frequency $\Gamma(m, \vec{x}, t)$. This is described by the next two terms of the population balance equation; again, there is a birth as well as a death contribution. $\gamma(m, m', \vec{x}, t)$ are the number of fragments with mass $m$ after breakup of a particle having mass $m'$. Finally, the term $r_m(\vec{x}, t)\delta(m - m_0)$ describes the rate of formation of nuclei with the smallest particle mass in the system ($m_0$).

Eqn. 2.6 describes the dynamics of the particle population $f(m, \vec{x}, t)$ for a laminar flow in the system and is also valid for a turbulent flow if we use the local instantaneous values of all variables. As we can see all variables involved may depend on the position $\vec{x}$ in the system and time $t$. Moreover, when the flow is turbulent all variables exhibit random fluctuations in time and space (Hinze, 1975). In the case of laminar flow there are no random fluctuations, so Eqn. 2.6 with appropriate boundary and initial conditions enables direct computation of the spatial distribution and temporal evolution of the particle population $f(m, \vec{x}, t)$. The population balance equation is solved along with the continuum transport equations for the continuous phase such as the differential momentum, mass, species, and energy balances. Of course appropriate models for the coagulation ($\beta(m, m', \vec{x}, t)$) and breakup kernels ($\Gamma(m, \vec{x}, t)$ and $\gamma(m, m', \vec{x}, t)$) need to be formulated. They depend on the size of the particle(s) involved but also on the local hydrodynamic conditions and in
particular for the coagulation kernel on the local concentrations of (ionic) species in the continuous phase.

In the case of turbulent flow the random fluctuations are accounted for by Reynolds decomposition (an instantaneous variable is split-up into its average and fluctuating part) and subsequent ensemble averaging:

\[
\frac{\partial f(m, x', t)}{\partial t} + \frac{\partial}{\partial m} \left[ g_m(m, x', t) f'(m, x', t) \right] + f(m, x', t) \frac{\partial g_m(m, x', t)}{\partial m} + g_m(m, x', t) \frac{\partial f(m, x', t)}{\partial m} +
\]

\[
\frac{v_i(m, x', t)}{\partial x_i} \frac{\partial f(m, x', t)}{\partial x_i} + f(m, x', t) \frac{\partial}{\partial x_i} \left[ v_i(m, x', t) \right] + \frac{\partial}{\partial x_i} [v_i'(m, x', t) f'(m, x', t)] =
\]

\[
\frac{1}{2} \int_{m_0}^m \beta(m - m', m', x', t) f(m - m', x', t) f(m', x', t) dm' - \int_m^\infty \Gamma(m', x', t) \gamma(m, m', x', t) f(m', x', t) dm' + \bar{c}(x', t) \delta(m - m_0)
\]

(an overbar is used to indicate an ensemble average). The resulting population balance equation contains several terms which call for closure schemes. The terms involved have been written in bold notation. Direct numerical simulations (DNS) may be used to include these fluctuations without the need for Reynolds decomposition, averaging, and subsequent closure, but unfortunately DNS for solving so complex problems is currently impossible. The divergence of the particle velocity field for both laminar (Eqn. 2.6) and turbulent flow (Eqn. 2.7) can in our application safely be neglected because we are considering very small particles with correspondingly small relaxation times.

For both laminar and turbulent flow the spatial distribution and temporal evolution of the particle population \( f(m, x', t) \) can be solved with the help of CFD-techniques. As an example Bakdyga and Orciuoli (1999) applied this technique to model particle precipitation in a turbulent flow field.

When it can be assumed that the system involved is homogeneous on the macroscale and that there are no random fluctuations we can take the average of the respective population balance equation (Eqn. 2.6) over the system domain. An example where this approach is usually followed is a well-mixed batch emulsion polymerization reactor where the system is, however, in reality not homogeneous. The consequence of this averaging over the system domain is that averaged coagulation and breakup kernels are used which therefore include the effect of possible spatial inhomogeneities of the rate of energy dissipation \( \epsilon \), number density function \( f(m, t) \), (ionic) species concentration in the continuous phase, etc. Moreover, in most cases the flow is turbulent so random fluctuations are present
which according to Eqn. 2.7 necessitate additional averaging and closure schemes.
The resulting averaged population balance equation for \( f(m,t) \) in the case of a homogeneous system without random fluctuations reads:

\[
\frac{\partial f(m,t)}{\partial t} + \frac{\partial}{\partial m} \left( g_m f(m,t) \right) = 12
\]

\[
\frac{1}{2} \int_{m_0}^{m} \beta(m-m',m') f(m-m',t) f(m',t) \, dm' - \int_{m_0}^{\infty} \beta(m,m') f(m',t) \, dm' - \Gamma(m) f(m,t) + \int_{m}^{\infty} \Gamma(m') \gamma(m,m') f(m',t) \, dm' + g_{m_0} \delta(m - m_0)
\]  

(2.8)

Thus, assuming an ideally mixed system the solution of Eqn. 2.8 yields the evolution of the particle size distribution \( f(m,t) \) in time and the coagulation and breakup kernels are the same as in Eqn. 2.6.

We usually work with Eqn. 2.8 keeping in mind the possible errors resulting from averaging.

In this work it was assumed that all particles are spherical, including the resulting coagulated ones. In other words, all the time we are considering a population of "singletons" having different sizes. So within this modeling framework the "doublet" formed by coagulation of two spherical particles having radii \( a_1 \) and \( a_2 \) has an equivalent radius of \( (a_1^3 + a_2^3)^{1/3} \). The formation of "triplets", "quadruplets", etc. is by successive mutual coagulation. Use of only particle radius for the internal coordinate \( \gamma \) implies that the structure of the aggregates formed is described in approximate form. Using fractal geometry the structure can be included in a simple way. However, this is only possible when there are many particles in the aggregate.

The time evolution of the characteristics of the latex dispersion can conveniently be expressed with the help of moments \( \mu_n \) of the number density function \( f(m,t) \):

\[
\mu_n(t) = \int_{m_0}^{\infty} m^n f(m,t) \, dm
\]

(2.9)

where \( n = 0, 1, 2, \ldots \). The zeroth moment \( \mu_0(t) \) represents the total number of polymer particles, the first moment \( \mu_1(t) \) the total mass of polymer particles in the system at time \( t \). Thus, the ratio of the first and the zeroth moment is the number averaged particle mass \( \overline{m}(t) \):

\[
\overline{m}(t) = \frac{\mu_1(t)}{\mu_0(t)}
\]

(2.10)

\[1\text{see Eqn. 2.14 later-on for the relation between particle size and mass}\]
Another important characteristic of a latex dispersion is the so-called polydispersity $P_d$ which gives an indication of the broadness of the particle size distribution:

$$P_d = \frac{\mu_2}{\mu_1^2}$$  \hspace{1cm} (2.11)

It is the ratio between the weight averaged particle mass ($\mu_2/\mu_1$) and the number averaged particle mass ($\mu_1$). A value of unity for $P_d$ corresponds to an infinitely narrow particle size distribution, i.e. the latex dispersion contains only particles with mass $\mu_1$. The variance $\sigma^2$ of the number density function $f(m, t)$ - equal to $\int_0^\infty (m - \mu_1)^2 f(m, t) dm$ - is related to the polydispersity in the following way:

$$\sigma^2 = \frac{\mu_2^2}{\mu_1^2} (P_d - 1)$$  \hspace{1cm} (2.12)

In this work perikinetic coagulation experiments were carried out using so-called "spent" latex dispersions which are the resulting latex dispersions after polymerization has finished. Consequently, the density of the polymer particles remains constant and as internal coordinate particle volume ($v$) can be used instead of mass ($m$). Coagulation was induced by the addition of a salt solution to the spent latex dispersion. Note that breakup will be neglected in the rest of this work since it is not operative under the experimental conditions chosen. Consequently, the population balance equation used to describe the temporal evolution of the particle size distribution simplifies to:

$$\frac{\partial f(m, t)}{\partial t} = \frac{1}{2} \int_{m_0}^{m} \beta(m - m', m') f(m - m', t) f(m', t) dm' - f(m, t) \int_{m_0}^{\infty} \beta(m, m') f(m', t) dm'$$  \hspace{1cm} (2.13)

where the number density function $f(m, t)$ is replaced by $f(v, t)$ in the case of coagulation of a spent latex dispersion.

The main focus in the next chapter will be on the development of a suitable model for the coagulation frequency $\beta(m, m')$ involving all three possible particle transport mechanisms, viz. Brownian diffusion of particles and convection of particles due to colloidal interaction and fluid motion.

Note that the use of particle mass as internal coordinate is more general since it can be used for both reacting and nonreacting systems. During an emulsion polymerization, when equilibrium swelling conditions prevail, a fraction $\phi^*$ of the particle volume is polymer with density $\rho_p$. Consequently, the average particle diameter $\bar{d}(t)$ can be calculated as

$$\bar{d}(t) = \left( \frac{6}{\mu_1(t)\pi (\phi^* \rho_p + (1 - \phi^*) \rho_0)} \right)^{1/3}$$  \hspace{1cm} (2.14)
where $\rho_m$ is the density of the monomer. All the particles, including the coagulated ones, are considered to be equivalent spheres. This assumption is reasonable since during an emulsion polymerization the particles are deformable and behave like droplets. As we will see later, during the coagulation experiments, the time evolution of the average particle size is followed with the help of dynamic light-scattering (see section 5.3.2). The obtained average particle size $R_h$ is the ratio of the sixth and the fifth moment of the particle radius distribution $f(r, t)$. Hence, the number density function $f(v, t)$, obtained from the PBE, has to be transformed into $f'(r, t)$ which is easily achieved since the expression relating particle volume and radius is monotonous ($v = \frac{4}{3}\pi r^3$). Returning to the population balance equation (Eqn. 2.8) for the batch emulsion polymerization reactor, we can set-up a mass balance for the amount of monomer $M(t)$ in the system at time $t$. Assuming that no monomer leaves the system by evaporation we obtain:

$$M_0 = M(t) + \int_{m_0}^{\infty} mf(m, t)dm$$  \hspace{1cm} (2.15)$$

where $M_0$ is the initial amount of monomer in the system. The integral term is the amount of monomer transformed into polymer due to polymerization.
Chapter 3

Governing equations describing relative particle motion and aggregation

We consider a dilute suspension subject to creeping flow and Brownian motion. The suspension contains small spherical particles freely dispersed in the Newtonian fluid; the dispersion is locally uniform and the local rate of energy dissipation does not vary in time and space. In what follows, the conditions briefly listed above, and their consequences for aggregation modeling, will be presented more precisely using mathematical relations and equations.

This work is restricted to binary interactions because for dilute suspensions the probability of a third particle disturbing the relative motion of two interacting particles is small; in fact one can define a "dilute suspension" as that in which the aggregation process is determined by the undisturbed binary encounters (dilute limit). We describe the process using an Eulerian approach. The coordinate system used to describe the binary interactions of the particles is sketched in Fig. 3.1. One of the two particles is taken as the central one, so motion and position of the other particle are expressed relative to this. The central particle has a radius $a_1$ and the other particle a radius $a_2 = \lambda a_1$ where $\lambda$ is the size ratio.

Note that due to the fact that the suspension is dilute and the particle size much larger than the scale of the "phenomenological point" (see Baldyga and Bourne, 1999), the concept of local concentration of particles does not make sense. Instead, we can use the conditional pair distribution function $p(\vec{r}, \lambda, t)$ which is defined in such a way that it corresponds to the number density of particles at position $\vec{r}$ from the center of the central particle with index "1". The conditional pair distribution function represents the pair probability function for the separation $\vec{r}$ between two particles. More precisely, $p(\vec{r}, \lambda, t)d\vec{r}$ represents the probability that the center of a particle with radius $a_2 = \lambda a_1$
Figure 3.1: Sketch of the geometry and of the spherical coordinate system used.

will be at time \( t \) in some volume element with radius \( d\tau \), centered at a distance \( \tau \) from the center of a particle with radius \( a_1 \). Let \( c_{2,\infty}(t) \) be the spatially homogeneous number density of particles with index "2" in the absence of aggregation. Then, integration over the system (or its spatially homogeneous region) gives:

\[
N_2(t) = \int_0^\infty \int_0^{2\pi} \int_0^{\pi} c_{2,\infty}(t) p(\tau, \lambda, t) d\tau d\lambda d\phi
\]

where \( N_2(t) \) refers to the total number of particles "2" in the system (or the well-defined region) at time \( t \). Eqn. 3.1 shows that the particle concentration (particle density) \( c_2(\tau, \lambda, t) = c_{2,\infty}(t)p(\tau, \lambda, t) \) can be indeed formally used instead of the appropriate pair distribution function. The particle pair distribution function (or the concentration distribution) depends on the relative motion of the particles and is governed by the following Fokker-Planck type balance equation:

\[
\frac{\partial c_2(\tau, \lambda, t)}{\partial t} + \nabla \cdot \mathbf{N} = R
\]

where \( \mathbf{N} \) is the particle flux vector and \( R \) stands for a source or sink term. Employing spherical coordinates the flux vector components are \( N_r, N_\theta \) and \( N_\phi \) in the radial, tangential, and azimuthal (circumferential) direction, respectively. The particle flux vector \( \mathbf{N} \) contains contributions by diffusion and convection and is given by:

\[
\mathbf{N} = -\overline{D} \cdot \nabla c_2(\tau, \lambda, t) + \mathbf{v} c_2(\tau, \lambda, t)
\]

where \( \overline{D} \) is the particle diffusion tensor and \( \mathbf{v} \) is the particle velocity vector. The contribution by Brownian diffusion will be discussed in section 3.2. The particle velocity vector
is the superposition of relative velocity induced by colloidal particle interactions and the relative velocity due to the fluid motion. Linear superposition of these velocities is allowed under assumption of creeping flow around the particles. In fact, for creeping (or Stokes) flow the nonlinear terms in the Navier-Stokes equations are negligible, because the inertia of the moving fluid is in that case negligible. The requirements for creeping flow translate into constraints for the values of two Reynolds numbers (see Sherman, 1990):

\[ Re = \frac{UL}{\nu} \ll 1 \quad \text{and} \quad \frac{AL^2}{U\nu} \ll 1 \]  

(3.4)

where it is supposed that the fluid motion is caused by a moving body with characteristic velocity \( U \), characteristic acceleration \( A \), and characteristic length \( L \). The second constraint expresses that the forces associated with acceleration of the moving body are negligibly small compared to the viscous friction. For colloidal particles the Reynolds numbers are in most cases much smaller than 1 since the characteristic length \( L \) can be identified with the particle size. In turbulent flow, colloidal particles are usually much smaller than the Kolmogorov microscale of the turbulence \( \lambda_K \):

\[ \lambda_K = \left( \frac{\nu^3}{\epsilon} \right)^{1/4} \]  

(3.5)

in which \( \epsilon \) is the local average rate of energy dissipation. We consider their interactions at distances much smaller than the Kolmogorov microscale:

\[ a_1 + a_2 \ll \lambda_K \]  

(3.6)

The relative particle velocity \( v_{12} \) at a distance \((a_1 + a_2)\) smaller than \( \lambda_K \) scales as:

\[ v_{12} \sim (a_1 + a_2) \sqrt{\frac{\epsilon}{\nu}} \]  

(3.7)

Hence, after substituting Eqn. 3.5 for \( \lambda_K \) and using Eqn. 3.7 for the characteristic velocity \( U \) one transforms Eqn. 3.6 to:

\[ Re = \left( \frac{a_1 + a_2}{\lambda_K} \right)^2 \sqrt{\frac{\epsilon}{\nu}} \ll 1 \]  

(3.8)

Regarding the second Reynolds number in Eqn. 3.4 we can estimate the characteristic acceleration \( A \) as the quotient of the Kolmogorov velocity \((\epsilon \nu)^{1/4}\) and time microscale \( \tau_K \) which is equal to \( (\nu^2/\epsilon)^{1/4} \). Substitution into Eqn. 3.4 yields \( \frac{a_1 + a_2}{\lambda_K} \ll 1 \) which is identical to Eqn. 3.6.

Thus, it is justified to make use of the creeping flow equations.
In the next section the relative particle velocity due to the fluid velocity field will be described in detail. Reason to start with the relative particle velocity and discuss Brownian diffusion and colloidal particle interaction in subsequent sections is that the relative particle velocity field determines the eventual symmetry of the situation considered.

### 3.1 Relative particle motion due to the fluid velocity field

Following Batchelor and Green (1972) the relative particle velocity due to an ambient fluid velocity field with deformation (rate of strain) tensor \( \overrightarrow{E} \) and rotation tensor \( \overrightarrow{\Omega} \) is denoted by \( \overrightarrow{\nu}(\overrightarrow{R}, \lambda) \) where \( \overrightarrow{R} \) is the vector connecting the centers of the two spheres and \( \lambda \) is their size ratio. To avoid confusion the fluid velocity field is written as \( \overrightarrow{v}^f(\overrightarrow{r}) \). The deformation tensor \( \overrightarrow{E} \), given by \( \overrightarrow{E} = \frac{1}{2}(\nabla \overrightarrow{v}^f + \nabla \overrightarrow{v}^f^T) \), describes fluid deformation\(^2\) and represents the symmetrical part of the fluid velocity gradient tensor \( \nabla \overrightarrow{v}^f \). The antisymmetrical part \( \frac{1}{2}(\nabla \overrightarrow{v}^f - \nabla \overrightarrow{v}^f^T) \) of the velocity gradient tensor is called rotation tensor \( \overrightarrow{\Omega} \) and corresponds to a solid-body rotation. \( \overrightarrow{\omega} \) denotes the angular velocity (or spin) vector and is given by \( \overrightarrow{\omega} = \frac{1}{2}(\nabla \times \overrightarrow{v}^f) \).

For the situation that on each sphere the resultant force and couple exerted by the hydrodynamic stress at the surface are zero, the relative particle velocity is described by the following equation (Batchelor and Green, 1972):

\[
\overrightarrow{\nu}(\overrightarrow{R}, \lambda) = \overrightarrow{\omega} \times \overrightarrow{R} + \overrightarrow{E} \cdot \overrightarrow{R} - \left\{ A(r, \lambda) \frac{\overrightarrow{R} \cdot \overrightarrow{R}}{r^2} + B(r, \lambda) \left( \overrightarrow{I} - \frac{\overrightarrow{R} \cdot \overrightarrow{R}}{r^2} \right) \right\} \cdot \overrightarrow{E} \cdot \overrightarrow{R} \tag{3.9}
\]

where \( \overrightarrow{I} \) is the unit second-order tensor. The first two terms \( \overrightarrow{\omega} \times \overrightarrow{R} + \overrightarrow{E} \cdot \overrightarrow{R} \) represent an undisturbed fluid velocity field (far away from the particles) which varies linearly with position. The last term involves the hydrodynamic interaction functions \( A(r, \lambda) \) and \( B(r, \lambda) \)\(^3\) and describes the disturbance of the ambient fluid velocity field caused by the presence of the two particles. Notice that Eqn. 3.9 can be used to describe particle movements in any flow field given by the rate of strain tensor \( \overrightarrow{E} \) and spin vector \( \overrightarrow{\omega} \). First we will consider as an example a simple shear flow and afterwards an axisymmetrical extensional flow field which is most appropriate to describe a turbulent flow field on the scale of aggregation for the particles considered.

For the simple shear flow the fluid velocity \( v_{L,3} \) varies in the \( x_2 \)-direction so the fluid velocity gradient tensor takes the simple form:

\[
\nabla \overrightarrow{v}^f = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & E_{23} \\ 0 & 0 & 0 \end{pmatrix} \tag{3.10}
\]

\(^2\)the superscript "T" indicates the transpose of a tensor

\(^3\)usually, the functions \( A(r, \lambda) \) and \( B(r, \lambda) \) are termed mobility functions
where $E_{23}$ is the shear rate. Splitting $\nabla \bar{\varepsilon}$ up into its symmetrical (the deformation tensor $\bar{E}$) and antisymmetrical part (the rotation tensor $\bar{\Omega}$) yields:

$$
\nabla \bar{\varepsilon}_L = \frac{1}{2} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & E_{23} \\ 0 & E_{23} & 0 \end{pmatrix} + \frac{1}{2} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & E_{23} \\ 0 & -E_{23} & 0 \end{pmatrix}
$$

This shows that a simple shear flow is the superposition of a pure straining and a pure rotational flow as sketched in Fig. 3.2.

With the help of Eqn. 3.9 we find the following relative velocity components for particles (Adler, 1981b) in terms of spherical coordinates $(r, \theta, \phi)$ which express the position of the sphere relative to a fixed rectangular coordinate system that is coincident with the center of the central particle:

$$
\begin{align*}
\nu_r &= \frac{\partial r}{\partial t} = \frac{E_{23}^2}{2} r (1 - A) \sin^2 \theta \sin 2\phi \\
\nu_\theta &= r \frac{\partial \theta}{\partial t} = \frac{E_{23}^2}{2} r (1 - B) \sin 2\theta \sin 2\phi \\
\nu_\phi &= r \sin \theta \frac{\partial \phi}{\partial t} = E_{23} r (\cos^2 \phi - \frac{B}{2} \cos 2\phi) \sin \theta
\end{align*}
$$

As already stated, the mobility functions $A = A(r, \lambda)$ and $B = B(r, \lambda)$ describe how the presence of both particles disturbs the ambient fluid velocity field. Notice that they are the same for any linear ambient fluid flow field. Concerning their behaviour we can write the following:

1. Because the particles cannot penetrate each other, the relative radial particle velocity $\nu_r$ is zero on the collision surface. Consequently, $A = 1$ for $r = a_1 + a_2$.

2. In general, the relative tangential velocity $\nu_\theta$ differs from zero on the collision surface because the particles can move over each other. Consequently, $B \neq 1$ for $r = a_1 + a_2$ except for the limit when one of the particles is much smaller than the other one (i.e. $\lambda \to 0$).
3. When the particles are far apart the relative particle velocities become equal to the undisturbed pure straining fluid velocities, i.e. \( A = B = 0 \) for \( r \to \infty \).

Appendix B discusses the derivation of the expressions used for the mobility functions \( A(r, \lambda) \) and \( B(r, \lambda) \).

As mentioned previously, particle aggregation is taking place on a scale smaller than the Kolmogorov microscale \( \lambda_K \) given by Eqn. 3.5. The two parameters governing the viscous fluid motion on this scale are the local average rate of dissipation of turbulent kinetic energy, \( \epsilon \), and the kinematic fluid viscosity \( \nu \). According to Batchelor (1980) a proper mechanistic view of turbulent fluid motion below the Kolmogorov scale is vortex stretching, which can be described as an axisymmetrical pure straining motion (extensional flow) with deformation tensor \( \overline{E} \):

\[
\overline{E} = \begin{pmatrix}
E_{11} & 0 & 0 \\
0 & E_{22} & 0 \\
0 & 0 & E_{33}
\end{pmatrix}
\]  

(3.13)

where for the diagonal elements we have \( E_{11} = E_{22} = -\frac{1}{2}E_{33} \) which satisfies the continuity equation \( \nabla \cdot \overline{v} = 0 \). \( E_{33} = <E_{\omega}> \) is the mean rate of extension of vortex lines (see Batchelor, 1980) in the direction of the vorticity vector and is given by:

\[
<E_{\omega}> = \frac{7}{6\sqrt{15}} \frac{\epsilon}{\nu} S \sqrt{\frac{\epsilon}{\nu}}
\]  

(3.14)

The multiplication factor arises because of the statistical distribution of the vorticity vector and has this particular value for turbulence which is locally homogeneous and isotropic. \( S \) is minus the "skewness factor" of the rate of extension in a fixed direction (that is, minus the mean cube of this rate of extension divided by the \( \frac{3}{2} \) power of its mean square). Batchelor (1980) estimated \( S \approx 0.6 \).

Imposing axisymmetry and, similar to the case of simple shear flow, employing Eqn. 3.9, we obtain for the relative particle velocity components in the radial and the tangential direction:

\[
\begin{align*}
\nu_r &= \frac{E_{33}r}{\nu}(1 - A)(3\cos^2\theta - 1) \\
\nu_\theta &= -\frac{3}{4}E_{33}r(1 - B)\sin 2\theta
\end{align*}
\]  

(3.15)

For reasons of simplicity \( \epsilon \) is written instead of \( E_{33} \). The mobility functions \( A(r, \lambda) \) and \( B(r, \lambda) \) for this elongational flow field were discussed previously for the simple shear flow field. A vector plot of the particle velocity field is sketched in Fig. 3.3. This graph includes the ambient fluid velocity field\(^4\).

\(^4\)by simply putting the mobility functions \( A \) and \( B \) to zero
Figure 3.3: Vector plot of the particle velocity field (in blue) as well as of the ambient fluid velocity field (in red).

It is seen that the velocity fields are similar (except the region close to the particle) and that the relative particle trajectories are around a sphere with radius equal to the sum of the radii of the particle pair, the so-called collision surface (or envelope). Fig. 3.4 clearly illustrates some other characteristics of the relative particle velocity field. The relative particle velocity is in the direction away from the central particle for $0 \leq \theta < \theta_{cr}$ and towards the central particle for $\theta_{cr} < \theta \leq \frac{\pi}{2}$. The critical angle $\theta_{cr}$, which corresponds to a relative particle velocity in the radial direction of zero, is equal to $\arccos\left(\frac{1}{\sqrt{3}}\right)$.

Figure 3.4: Illustration showing some characteristics of the relative particle velocity field.
### 3.2 Brownian diffusion

Due to random thermal motion of the molecules of the dispersing medium, a particle with radius $a_i$ makes a random walk. Einstein (1905) described this Brownian motion as diffusion of the particle with a diffusion coefficient:

$$D_i^\infty = \frac{k_B T}{6 \pi \mu a_i}$$

(3.16)

in which $k_B$ is the Boltzmann constant, $T$ the (absolute) temperature, and $\mu$ the dynamic fluid viscosity.

When a binary system is considered and the separation between the two particles is large, a mutual diffusion coefficient $D_{12}^\infty$ must be used to describe the relative motion since both particles are diffusing independently:

$$D_{12}^\infty = D_1^\infty + D_2^\infty = \frac{k_B T}{6 \pi \mu} \left( \frac{1}{a_1} + \frac{1}{a_2} \right)$$

(3.17)

However, when they are close to each other, due to the presence of both particles the mutual diffusion coefficient is reduced by hydrodynamic interaction (viscous resistance caused by squeezing of fluid between the two solid particles) and becomes a function of the center-to-center distance $r$ and the size ratio $\lambda = \frac{a_2}{a_1}$. In other words, the mutual diffusion coefficient is a function of distance as well as of geometry. In addition to this the mutual diffusion coefficient is not the same in every direction so instead we use a mutual diffusion tensor $\bar{D}(\vec{r}, \lambda)$ where $\vec{r}$ is the vector from the center of the central particle to that of the second particle. The expression for the mutual diffusion tensor derived by Batchelor (1976) is:

$$\bar{D}(\vec{r}, \lambda) = D_{12}^\infty \left\{ G(r, \lambda) \frac{\vec{r} \cdot \vec{r}}{r^2} + H(r, \lambda) \left( I - \frac{\vec{r} \cdot \vec{r}}{r^2} \right) \right\}$$

(3.18)

where the center-to-center distance $r$ is equal to the length of the vector $\vec{r}$. The hydrodynamic interaction functions $G(r, \lambda)$ and $H(r, \lambda)$ are due to the fluid squeezing between the two particles. In this study only the mutual diffusion component in the radial direction ($D_r$) was used in the computations. The hydrodynamically hindered diffusion in the radial direction is expressed using the hydrodynamic interaction function $G(r, \lambda)$, so that $D_r(r, \lambda) = G(r, \lambda)D_{12}^\infty$. The behaviour of $G(r, \lambda)$ is such that $G$ is zero when the particles touch (solid particles) and approaches 1 when they are far apart (no hydrodynamic hindrance). This kind of dependence was first introduced into the expression for the perikinetic rate of aggregation by Derjaguin and Muller (1967) and their conclusion was that it is essential to include it. In appendix A a derivation is given of the expression.
used in this study for $G(r, \lambda)$.

Similarly, the tangential mutual diffusion coefficient is written as $D_{\theta}(r, \lambda) = H(r, \lambda)D_{\theta}^{\infty}$.

Note, however, that in general $H$ is not zero when the particles touch because they can still move over each other along their surface (parallel to their plane of contact, but not perpendicular to it). The reader is referred to appendix A and Fig. 3.7 for more information on $H(r, \lambda)$.

### 3.3 Colloidal interaction

Due to their colloidal nature the particles are subject to a potential energy field of interaction $\psi(r)$. The corresponding relative particle velocity for creeping flow is calculated using the following equation derived by Spielman (1970):

$$
\psi_{\text{rel}} = -\frac{D_{r}}{k_{B}T} \frac{\partial \psi}{\partial r}
$$

where $D_{r}$ is the mutual diffusion coefficient in the radial direction (see section 3.2). In the case where spherical symmetry for the potential energy of interaction is assumed, $\psi$ varies in the radial direction only. One might wonder why the expression for the relative particle velocity contains a diffusion coefficient. The reason is that the friction between the particles and the surrounding fluid balances the colloidal force of interaction. This friction is directly coupled to diffusion as expressed by the generalized Stokes-Einstein expression.

The potential energy of interaction can be attributed to many different sources. The most important interparticle forces and their origins are listed below:

1. Forces arising from the electromagnetic fluctuations of the matter; these forces are called van der Waals forces and are always attractive when two identical (same material) particles are considered.

2. Electrostatic forces arising from the cloud of counterions surrounding the colloidal particles. This cloud of counterions is present because the polymer particles consist of polymer chains with ionic endgroups, but mainly because of the ionic part of the adsorbed surfactant molecules. These forces are in most cases repulsive.

3. Born forces are repulsive forces of extremely short range. They occur when two atoms or molecules are so close together that their electron clouds start to overlap.
4. Steric forces depend on the kind of molecules adsorbed on the surface of the particles and on their conformation. Depending on the free energy of mixing between these adsorbed molecules and the solvent medium these forces can be both repulsive and attractive.

Since in this study we are dealing with polymeric latices that are stabilized by ionic emulsifiers, forces 1. and 2. are largely dominant. Therefore, the latter two forces will be neglected. Moreover, they are either not well understood or modelled, or only relevant for extremely short interparticle distances. For this reason the total energy of interaction \( \psi(r) \) will be calculated as the sum of an attractive van der Waals \( \psi_{\text{att}}(r) \) and a repulsive electrostatic contribution \( \psi_{\text{rep}}(r) \).

3.3.1 The attractive potential energy of interaction

The attractive potential energy of interaction \( \psi_{\text{att}}(r) \) between two spherical particles finds its origin in so-called van der Waals forces between the neutral atoms or molecules the particles consist of. Three different types of this force are distinguished.

First, Keesom attraction which is due to the presence of a permanent electric dipole moment in polar molecules. By averaging over all orientations of the two molecules it is found that there is a net attraction. Furthermore, a permanent dipole induces a dipole moment in a nonpolar molecule. This results in the second, so-called Debye attraction between the permanent and the induced dipole. The third type of van der Waals forces is between two neutral nonpolar molecules. Each of them forms a dipole that continuously fluctuates in direction and magnitude. Consequently there is a net attraction between the two induced dipoles.

The attractive potential energy of two spherical particles is obtained by adding the contributions of all possible pairs of molecules. This can be accomplished by integrating over the interior volume of both spherical particles. The resulting expression for \( \psi_{\text{att}}(r) \) was first obtained by Hamaker (1937):

\[
\psi_{\text{att}}(r) = -\frac{Ha}{6} \left[ \frac{2a_1a_2}{r^2 - (a_1 + a_2)^2} + \frac{2a_1a_2}{r^2 - (a_1 - a_2)^2} + \ln \left( \frac{r^2 - (a_1 + a_2)^2}{r^2 - (a_1 - a_2)^2} \right) \right]
\]

where \( Ha \) is the Hamaker constant.

The electromagnetic interactions of the pairs of molecules are assumed to be transmitted instantaneously. However, in reality it takes a finite time for an electromagnetic signal
to travel back and forth between the molecules. Because of this, the van der Waals force is weakened (or retarded) when the molecules are far apart. With the help of quantum mechanics this retardation effect can be taken into account (Casimir and Polder, 1948) and the resulting equation for the potential energy of attraction is known as the CLM equation (Clayfield, Lumb and Mackey, 1971). A simple estimate for the retarded van der Waals force was derived by Schenkel and Kitchener (1960).

In this study the original Hamaker expression (Eqn. 3.20) is used since differences due to retardation effects are observed only for relatively large separation distances with no effect on aggregation in our case.

3.3.2 The repulsive potential energy of interaction

Colloidal polymer particles have electrostatic charges on their surface. This is due to ionic endgroups of the polymer chains (because of the initiator used during emulsion polymerization) but the main contribution is by the ionic part of surfactant molecules adsorbed on the surface of the polymer particles. The surfactant molecules have a nonpolar tail which is in close contact with the polymer particle surface and an ionic head which prefers the aqueous side. The requirement of macroscopic electrical neutrality implies that there will be a concentration of counterions from the solution and the formation of the so-called electrical double layer around each particle. The potential energy of repulsion $\psi_{\text{rep}}(r)$ for a pair of particles is due to electrostatic repulsion when these double layers overlap. A closer look at the Stern layer shows that it can be subdivided into two regions: an inner layer occupied by specifically adsorbed counterions that are unhydrated or partially hydrated, and a second layer where hydrated counterions are located. The boundaries of these regions are often known as the inner Helmholtz plane (IHP) and outer Helmholtz plane (OHP). Outside this plane is the diffuse layer. Fig. 3.5 gives an overview of the different regions that are distinguished in the Stern layer and shows also the neighbouring electrical double layer surrounding the polymer particles. As we will see afterwards, the electric potential at the OHP ($\Phi_d$) is needed to calculate the potential energy of repulsion for a pair of particles. The electrokinetic shear boundary where we measure the zeta potential $\zeta$ is thought to lie just outside the OHP and therefore it is reasonable to assume that $\Phi_d \approx \zeta$. Note that the surfaces of the polymer particles are assumed to be smooth. Moreover, in the following of this work we will always employ absolute values of electric potentials and surface charge densities.

The ionic parts of the surfactant molecules adsorbed on the polymer surface result in
Figure 3.5: Overview of the structure of the Stern layer and of the neighbouring electrical double layer.

A surface charge density $\sigma_0$ and the corresponding electric potential on the particle surface is $\Phi_0$. The surface charge density $\sigma_0$ is calculated as:

$$\sigma_0 = z_j e \gamma N_{mol}$$

(3.21)

where $\gamma$ is the emulsifier surface concentration ($\text{mg}^2$/$\text{m}^2$) on the polymer particle and $z_j$ is the valence of the adsorbed surfactant molecules. The calculation of $\gamma$ will be discussed separately in section 5.3.5.

In the inner part of the Stern layer, i.e. between the particle surface and the IHP, specific adsorption of counterions occurs. This is called adsorption of the second kind. The adsorbed counterions (surface concentration $\gamma_i$) carry a surface charge $\sigma_i$ which corresponds to an electric potential $\Phi_i$. An onset for the description of the counterion adsorption equilibrium was given by Lyklema (1989) in the case of a single counterion. He proposed to use a Langmuir isotherm modified to account for the electrostatic effects:

$$\frac{\gamma_i}{\gamma} = \frac{K c_{i,\infty} \exp \left(\frac{z_i e \Phi_i}{k_B T}\right)}{1 + K c_{i,\infty} \exp \left(\frac{z_i e \Phi_i}{k_B T}\right)}$$

(3.22)

where $K$ is the Langmuir constant for counterion adsorption, while $c_{i,\infty}$ and $z_i$ are the bulk concentration and the valence of the counterion, respectively. Since surface concentration
and charge are directly related, the ratio on the left-hand side of Eqn. 3.22 is equal to $\frac{\sigma_i}{\sigma_0}$.

The layer between IHP and OHP, whose thickness is approximately equal to the radius of a solvated counterion, is charge free and hence works like a molecular condenser. Consequently, the surface charge density at the OHP, $\sigma_d$, is the same as at the IHP and is calculated as the net surface charge density:

$$\sigma_d = \sigma_0 - \sigma_i \tag{3.23}$$

Another consequence is that the electric potential drops linearly between the IHP and the OHP, leading to the relation:

$$\Phi_i - \Phi_d = \sigma_d \frac{\delta}{\epsilon_S} \tag{3.24}$$

where $\delta$ stands for the outer Stern layer thickness and $\epsilon_S$ indicates the permittivity of the outer Stern layer. $\epsilon_S$ is taken as equal to the permittivity of water thus neglecting dielectric saturation effects.

In addition to Eqs. 3.21-3.24 an equation is needed to determine all surface charge densities and electric potentials of the Stern layer and the electric double layer surrounding the colloidal particle. This additional equation will be the relation between surface charge density $\sigma_d$ and electric potential $\Phi_d$ which is a consequence of the model describing the diffuse layer which will now be described.

To model the repulsive potential energy of interaction $\psi_{rep}(r)$ it is necessary to ascertain how the ions are distributed around a colloidal particle in the diffuse part of the electrical double layer (see for instance Hiemenz, 1986). For this purpose the number distribution $n_i$ for ions of type $i$ is written according to Eqs. 3.2 and 3.3. Assuming a (quasi) steady-state, we obtain for the number of ions $i$ per unit volume of the solution:

$$\nabla \cdot (D_i \nabla n_i) - \nabla \cdot (u_i n_i) = 0 \tag{3.25}$$

where $D_i$ is the diffusion coefficient of ion $i$ and $u_i$ is the ion velocity caused by the electrical field that acts on the ions. Employing an analogue expression like Eqn. 3.19 for ions with valence $z_i$ we obtain:

$$\nabla \cdot \left[ \nabla n_i + n_i \frac{z_i e}{k_B T} \nabla \psi \right] = 0 \tag{3.26}$$

The analytical solution to Eqn. 3.26 for both spherical and flat particles is known as the Boltzmann distribution:

$$n_i = n_{i,\infty} \exp \left( -\frac{z_i e \psi}{k_B T} \right) \tag{3.27}$$
where \( n_i,\infty \) is the number concentration of ion \( i \) in the bulk of the solution.

We can combine this with the Poisson equation which is the relation between charge density \( \rho \) and potential \( \psi \):

\[
\nabla^2 \psi = \frac{-\rho}{\epsilon} \tag{3.28}
\]

where \( \epsilon \) is the permittivity of the dielectric medium. Since the charge density \( \rho \) is simply \( \sum_i n_i z_i e \) we obtain the so-called Poisson-Boltzmann equation:

\[
\nabla^2 \psi = -\frac{e}{\epsilon} \sum_i n_i,\infty z_i \exp \left( -\frac{z_i e \psi}{k_B T} \right) \tag{3.29}
\]

Macroscopic electroneutrality in the electrical double layer implies that the surface charge density \( \sigma_d \) at the OHP can be found by integration of the charge density \( \rho \) in Eqn. 3.28 from 0 (at the OHP) to \( \infty \). Using the Debye-Hückel expression for \( \psi(r) \) we obtain:

\[
\sigma_d = \frac{a}{\epsilon} \frac{\kappa a}{1 + \kappa a} \tag{3.30}
\]

In this equation \( a \) is the radius of the particle and \( \kappa \) is the so-called Debye-Hückel constant which is inversely proportional to the thickness of the electrical double layer and is given by:

\[
\kappa = \sqrt{\frac{2 e^2 N_A e I}{e k_B T}} \tag{3.31}
\]

where \( I \) is the ionic strength calculated as \( \frac{1}{2} \sum_i z_i^2 c_i,\infty \), \( c_i,\infty \) being the bulk concentration of ions of type \( i \). \( N_Ae \) is the Avogadro number and \( e \) is the charge of an electron. Eqn. 3.30 is used as the additional equation required to relate surface charge density and electric potential.

In the literature there is a large number of expressions available for the potential energy of repulsion of a pair of colloidal particles due to overlap of their electrical double layers (see Elimelech et al. (1995) for a comprehensive overview). Their ranges of applicability depend on the dimensionless thickness of the electrical double layer \( (\kappa a) \) and on the absolute values of the surface potentials \( \Phi_d \) of the two particles. In this study we employed the frequently used Hogg-Healy-Fürstenau expression (Hogg et al., 1966) which, strictly speaking, applies only to thin double layers \( (\kappa a > 1) \) but predicts reasonably accurate values of \( \psi_{\text{rep}} \) even for values of \( \Phi_d \) up till 50 – 60 mV. The expression for \( \psi_{\text{rep}} \) reads:

\[
\psi_{\text{rep}}(r) = \frac{\pi e a_1 a_2 (\Phi_{d,1}^2 + \Phi_{d,2}^2)}{(a_1 + a_2)} \left[ \frac{2 \Phi_{d,1} \Phi_{d,2}}{(\Phi_{d,1}^2 + \Phi_{d,2}^2)} \ln \left( \frac{1 + \exp(-\kappa \Phi_{d,1})}{1 - \exp(-\kappa \Phi_{d,1})} \right) + \ln \left( 1 - \exp(-2\kappa \Phi_{d,1}) \right) \right] \tag{3.32}
\]
in which $h_1 = r - a_1 - a_2$ is the surface-to-surface distance between the two particles.

Note that the colloidal repulsion is calculated here under the assumption of a constant value of the surface potential $\Phi_d$ during approach. However, electrical double layer interactions can occur such that either the surface potential $\Phi_d$ or the surface charge density $\sigma_d$ remains constant. If particle-particle encounters are sufficiently slow, redistribution of the surface charge will maintain an electrostatic equilibrium, and hence the surface potential remains constant. However, the other limiting case is based on the argument that during the time scale of a Brownian encounter, the diffusion of ions necessary to maintain electrostatic equilibrium is not fast enough so that encounters will occur at constant surface charge rather than constant surface potential. The right approach should be based on a full description of the evolution of the ionic equilibria during approach along with the Poisson-Boltzmann equation and this forms the basis of the proposed "charge regulation" theory, as discussed by Behrens and Borkovec (1999). However, in this work all these aspects are neglected and the calculations were performed for the frequently adopted limiting case of constant surface potential.

### 3.4 The complete convection-diffusion equation

Employing spherical coordinates (see Fig. 3.1) the complete convection-diffusion equation (Eqn. 3.2) in terms of particle fluxes reads:

\[
\frac{\partial c_2(r, \theta, \phi, t)}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 N_r c_2 \right) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} \left( N_\theta c_2 \sin \theta \right) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} \left( N_\phi c_2 \right) = 0 \quad (3.33)
\]

With the help of Eqn. 3.3 this equation can be expressed completely in terms of the particle concentration $c_2(r, \theta, \phi, t)$. For reasons of convenience from now on we simply write $c_2$ for the particle concentration $c_2(r, \theta, \phi, t)$. The resulting equation reads:

\[
\frac{\partial c_2}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \left[ v_r + v_{r, int} \right] c_2 \right) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \left[ v_\theta c_2 - \frac{D_\theta}{r} \frac{\partial c_2}{\partial \theta} \right] \right) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} \left( v_\phi c_2 - \frac{D_\phi}{r} \frac{\partial c_2}{\partial \phi} \right) = 0 \quad (3.34)
\]

The divergence of the particle velocity terms in Eqn. 3.34 is not equal to zero because the clouds of particles are compressible especially when the particles are close to each other. This is contrary to the population balance equations (Eqns. 2.6 and 2.7) where the divergence can usually be assumed to be equal to zero. To calculate the coagulation rate $Q$ we can use the (quasi) steady-state solution of Eqn. 3.34 provided that three conditions
are satisfied.

First, the characteristic time of the controlling mechanism must be significantly shorter than the Lagrangian time microscale $\tau_L$, which is an estimate for the lifetime of the structure with creeping flow in a turbulent flow field. Furthermore, the characteristic time for coagulation $\tau_{1/2}$ has to be much larger than the Lagrangian time microscale $\tau_L$ so the change of $c_{2,\infty}$ during $\tau_L$ is negligible. Finally, the nature of the colloidal interaction forces must satisfy the requirements for existence of a steady-state solution of the convection-diffusion equation (Van de Ven and Mason, 1977b). Let us further discuss all these aspects in some detail.

The Lagrangian time microscale $\tau_L$ (see Baidyga and Bourne, 1995) is given by:

$$\tau_L = Re^{1/2}\frac{\lambda_g}{u'} = Re^{1/2}\frac{\sqrt{\nu}}{\epsilon} = Re^{1/2}\tau_K$$

(3.35)

where $Re_{\lambda_g} = \frac{u'\lambda_g}{\nu}$ in which $\lambda_g$ is the Taylor microscale and $u'$ are the turbulent rms (root mean square) velocity fluctuations. $\tau_K$ is the Kolmogorov time microscale. To make an estimate for $Re_{\lambda_g}$ we can express it in terms of $Re_L$ which is the Reynolds number of the large energy-containing eddies with characteristic size $L$ ($Re_L = \frac{u'L}{\nu}$). $L$ is usually proportional to the size of the element which introduces the kinetic energy into the system. For instance, in a stirred vessel equipped with a Rushton turbine agitator, $L$ is roughly half of the impeller height and for a pipe flow half of the pipe radius. The reason being that because of symmetry in a pipe cross section there can be two eddies. The scale $L$ of an eddy is related to its radius. Experimentally, $L$ can be determined using simultaneous velocity measurements at two points at various distances and calculating the velocity correlation coefficient. $Re_{\lambda_g}$ and $Re_L$ can be related with the help of the following two expressions for the rate of dissipation of turbulent kinetic energy (see Hinze, 1975):

$$\epsilon = 15\nu\frac{u'^2}{\lambda_g^3} = B\frac{u'^3}{L}$$

(3.36)

These are valid for isotropic, homogeneous turbulence and reflect the transport of turbulent kinetic energy from the large energy-containing eddies to the smallest ones (energy cascade) where it is dissipated by viscous stresses. The constant of proportionality $B$ is of order 1. Utilizing Eqn. 3.36 we derive:

$$Re_{\lambda_g} = Re_L^{1/2}\sqrt{\frac{15}{B}}$$

(3.37)

Notice that the turbulent rms velocity fluctuations $u'$ can be estimated using Eqn. 3.36 as $\left(\frac{\epsilon L}{B}\right)^{1/3}$. 


Regarding the first condition we distinguish two situations.

When Brownian diffusion of particles is controlling (*perikinetic coagulation*), the particle Péclet number defined as:

\[ Pe = \frac{\left( \frac{\alpha}{\alpha_0} \right)^{1/2} \alpha^2}{D^{\infty}} \]  

is much smaller than unity. We have introduced \( a = \frac{a_1 + a_2}{2} \) as characteristic length to keep the same form of the complete dimensionless convection-diffusion equation for unequal-sized particles as Feke and Schowalter (1983) used for equal-sized particles (further details about this are to be found at the end of this section). \( D^{\infty} \) is obtained by putting \( a_1 \) and \( a_2 \) in Eqn. 3.17 for \( D^{\infty}_{1/2} \) equal to \( a \).

However, for the situation when relative particle motion due to fluid flow is controlling (*orthokinetic coagulation*), the particle Péclet number is much larger than unity.

The characteristic time for Brownian diffusion \( \tau_B \) is:

\[ \tau_B = \frac{\alpha^2}{D^{\infty}} \]  

Hence, the condition \( \tau_B \ll \tau_L \) can be written as:

\[ Pe \ll \frac{1}{Re_L^{1/4}} \left( \frac{15}{B} \right)^{1/4} \]  

This condition is satisfied when the fluid flow is turbulent since then \( Re_L \gg 1 \).

For the situation when particle motion due to fluid flow is controlling, the characteristic time of elongation \( \tau_E \) has to be much smaller than the Lagrangian timescale. \( \tau_E \) is inversely proportional to the rate of deformation \( E_{33} \) given by Eqn. 3.14. Hence, the requirement \( \tau_E \ll \tau_L \) can be written as:

\[ Re_{E_{\lambda}} \sqrt{\frac{\nu}{c}} \gg \frac{1}{E_{33}} \approx \frac{1}{0.18} \sqrt{\frac{\nu}{c}} \]  

or simply \( Re_{E_{\lambda}} \gg 30 \) which, using Eqn. 3.37, corresponds to \( Re_L \gg 60 \). Again, this condition is satisfied for a turbulent flow.

The characteristic time for coagulation can be estimated as the time needed to reduce the number of particles in the system to half of its original value \( N_{2,0} \). When the coagulation frequency is \( \beta \) we obtain:

\[ \tau_{1/2} = \frac{1}{\beta N_{2,0}} \]  

\( ^{\text{we can also use } E_{33} \text{ (or } E) \text{ instead of } \sqrt{\frac{\nu}{c}} \text{ because of their proportionality according to Eqn. 3.14}} \)
Therefore, using Eqns 3.35 and 3.37 the requirement $\tau_{1/2} \gg \tau_L$ can be written as:

$$\frac{1}{\beta N_{2,0}} \gg Re^{1/4} \left( \frac{15}{B} \right)^{1/4} \sqrt{\frac{\nu}{\epsilon}}$$  \hspace{1cm} (3.43)

This condition is fulfilled especially because for all cases considered the coagulation frequency $\beta$ is low and the Lagrangian time microscale $\tau_L$ short.

The requirements given by van de Ven and Mason (1977b) for existence of a steady-state of the convection-diffusion equation are the following:

1. Denoting $h = \frac{r - a_1 - a_2}{a_1}$ as the dimensionless gap between the two particles, the first requirement on the potential energy of interaction can be written as:

$$\lim_{h \to 0} \frac{1}{h} \frac{\partial \psi(r)}{\partial h} = 0 \hspace{1cm} (3.44)$$

This closely resembles the requirement for two spheres approaching each other in an axisymmetric force field to come into contact in a finite time.

2. The second requirement is that the potential energy of interaction vanishes when the two particles are far apart:

$$\lim_{r \to \infty} \psi(r) = 0 \hspace{1cm} (3.45)$$

For the DLVO-type of colloidal interaction forces considered in this work both requirements are always satisfied.

The conclusion is that the assumption of a (quasi) steady-state is always justified when coagulation in a turbulent flow field is considered. For this reason the first term $\frac{\partial \psi_1}{\partial t}$ in the convection-diffusion equation (Eqn. 3.34) is omitted.

After solving the partial differential equation for $c_2(r, \theta, \phi)$, the aggregation rate $Q$ is found by integration of the radial particle flux $N_r$ over the surface of the central particle:

$$Q = 2 \int_0^{\pi/2} \int_0^{2\pi} r^2 \sin \theta \left[ (v_r + v_{r, \text{int}}) c_2 - D_r \frac{\partial c_2}{\partial r} \right]_{r = a_1 + a_2} d\theta d\phi \hspace{1cm} (3.46)$$

The factor 2 arises because there are two hemispheres.

In the subsequent sections several limiting and further simplified cases of Eqn. 3.34 will be discussed. For this reason the different terms have been indicated with a number surrounded with a box such as $[2]$. Three different kinds of cases will be distinguished, viz. perikinetic coagulation ($Pe = 0$), orthokinetic coagulation ($Pe \gg 1$), and coagulation with both a peri- and an orthokinetic contribution.
3.5 Dimensionless representation

It is useful to introduce few other dimensionless groups besides the Péclet number (Eqn. 3.38) and the size ratio λ which characterizes the geometry.

The ratio between repulsive and attractive potential of interaction can be expressed using the repulsion number \( R_p \):

\[
R_p = \frac{e \Phi_{d,1}^2 a}{H_a}
\]

where the electric surface potential \( \Phi_{d,1} \) at the OHP is assumed to be equal to the zeta potential \( \zeta \) (see Fig. 3.5) and \( H_a \) is the Hamaker constant (which occurs in Eqn. 3.20).

The ratio between the surface potentials of the two particles is expressed as:

\[
\Phi = \frac{\Phi_{d,2}}{\Phi_{d,1}}
\]

The so-called flow number is a measure of the importance of viscous flow relative to interparticle attraction:

\[
Fl = \frac{3\pi \mu a^3 E_{33}}{H_a} = \frac{k_B T}{H_a} \tilde{P} = \tilde{P}^{-1} \tilde{P}
\]

where \( \tilde{H}_a \) is the dimensionless\(^6\) Hamaker constant:

\[
\tilde{H}_a = \frac{H_a}{k_B T}
\]

To render the complete convection-diffusion equation (Eqn. 3.2 coupled with the particle flux vector \( \vec{N} \) given by Eqn. 3.3) dimensionless, the different quantities involved are scaled. Lengths are scaled on \( a \), velocities on \( E \cdot a \), diffusivities on \( \frac{k_B T}{3\pi \mu a} \), and forces on \( \frac{H_a}{a} \). The result, as given by Feke and Schowalter (1983) for equal-sized particles, is:

\[
\nabla \cdot \left[ \left( \nabla + \frac{1}{Fl} \vec{D} \cdot f_{r, int} \vec{e}_r \right) p \right] = \frac{1}{P_e} \nabla \cdot \left[ \vec{D} \cdot \nabla \tilde{p} \right]
\]

where \( p \) is the conditional pair distribution function which can be replaced by the particle concentration \( c_2 \). \( \vec{e}_r \) represents a unit vector along the line connecting the centers of the two particles. \( f_{r, int} \) is the dimensionless colloidal force of interaction in the direction of \( \vec{e}_r \) and is split-up in the following way:

\[
f_{r, int} = f_{att} + R_p f_{rep}
\]

where \( f_{att} = \frac{\partial \Phi_{att}}{\partial r} \) and \( f_{rep} = \frac{\partial \Phi_{rep}}{\partial r} \) are the attractive and repulsive colloidal force of interaction, respectively.

\(^6\) A tilde refers to a dimensionless quantity.
3.5.1 Perikinetc coagulation

Part A

The first simplified case was obtained in the classical paper by Smoluchowski (1917) and is called **fast coagulation**. There is neither fluid motion (terms 2, 5, and 7) nor colloidal interaction (term 3). Hence, \( Pe = Fl = 0 \) and because of spherical symmetry only the Brownian diffusion term 4 in the radial direction remains. There are no attractive colloidal forces considered, but instead it is assumed that each particle that diffuses up to the collision surface coagulates. Viscous particle interactions are not accounted for (i.e. \( G = 1 \)) so the convection-diffusion equation takes the simple form:

\[
\frac{d}{dr} \left( r^2 D_{12} \frac{dc_2}{dr} \right) = 0
\]

(3.53)

with boundary conditions \( c_2 = 0 \) for \( r = a_1 + a_2 \) and \( c_2 = c_{2,\infty} \) when \( r \to \infty \). Consequently, using Eqn. 3.46 we find that the rate of coagulation for fast coagulation is:

\[
Q = 4\pi D_{12}^{\infty}(a_1 + a_2)c_{2,\infty}
\]

(3.54)

Part B

We call **slow coagulation** when the coagulation takes place under the influence of Brownian diffusion and colloidal interaction (terms 3 and 4 in the convection-diffusion equation). It was first investigated by Fuchs (1936). Similar to the previous part of this section viscous particle interactions were not included (so \( G = 1 \)). Again, there is spherical symmetry and no fluid motion thus the governing equation for the particle concentration \( c_2(r) \) becomes:

\[
\frac{d}{dr} \left[ r^2 \psi_{r, int} c_2 - D_{12}^{\infty} \frac{dc_2}{dr} \right] = 0
\]

(3.55)

This ordinary, second-order differential equation for \( c_2(r) \) is solved imposing the boundary conditions \( c_2 = 0 \) for \( r = a_1 + a_2 \) and \( c_2 = c_{2,\infty} \) for \( r \to \infty \). The rate of coagulation \( Q \) is then calculated with the help of Eqn. 3.46 to yield:

\[
Q = \frac{4\pi D_{12}^{\infty}(a_1 + a_2)c_{2,\infty}}{W}
\]

(3.56)

where the denominator \( W \) is usually called the **stability ratio** and is given by:

\[
W = (a_1 + a_2) \int_{a_1 + a_2}^{\infty} \frac{c_{2,\infty}}{r^2} dr
\]

(3.57)

It is seen that \( W \) is the ratio between the rate for fast coagulation \( 4\pi D_{12}^{\infty}(a_1 + a_2)c_{2,\infty} \) (see the previous part) and the coagulation rate \( Q \) for slow perikinetc coagulation. As expected, when no colloidal particle interaction forces are operative (i.e. \( \psi(r) = 0 \)) the stability ratio \( W \) approaches 1 and we obtain the fast coagulation rate expression.
Part C

Derjagnin and Muller (1967) and Spielman (1970) included the reduction of the mutual diffusion coefficient $D_{ij}^{m}$ by fluid squeezing. Hence, the hydrodynamic interaction function $G(r, \lambda)$ differs from 1. The same terms of the convection-diffusion equation as in part B of this section were accounted for. For this case attractive colloidal forces must be present so $\tilde{H}a > 0$, and as for the previous two parts $Pe = Fl = 0$.

Contrary to the previous two simplified cases this is a real limiting case. The expression for the rate of coagulation is very similar to the one in the previous part:

$$Q = \frac{4\pi D_{ij}^{m}(a_1 + a_2)c_{2,\infty}}{W}$$

but the stability ratio $W$ is corrected and now includes the hydrodynamic interaction function $G(r, \lambda)$:

$$W = (a_1 + a_2) \int_{a_1+a_2}^{\infty} \frac{\exp\left(\frac{\psi(r)}{k_BT}\right)}{G(r, \lambda)r^2} dr$$

3.5.2 Orthokinetic coagulation

Part A

For this simplified case only relative particle motion due to fluid flow (term $\frac{2}{2}$ in Eqn. 3.34) leads to coagulation. No colloidal forces are operative and Brownian diffusion in the radial direction is negligible compared to the relative particle motion due to fluid flow ($Pe^{-1} = 0$). For a simple shear flow the relative particle velocity in the radial direction $\nu_r$ is given by Eqn. 3.12. When the mobility function $M$ is assumed to be 0 the particle concentration is $c_{2,\infty}$ everywhere and particle trajectories may cross the collision surface at $r = a_1 + a_2$ which leads to coagulation. For this reason we can obtain the rate of coagulation with the help of Eqn. 3.46 and integrate in the region where $\nu_r$ is directed towards the central particle:

$$Q = \frac{4}{3}(a_1 + a_2)^3 E_{23} c_{2,\infty}$$

Smoluchowski (1917) obtained the same result by dividing a sphere with radius $R$ in slices with thickness $dx_2$ (see Fig. 3.6).

Realizing that the fluid velocity equals $x_2 \frac{\partial v_{L,3}}{\partial x_2}$ integration yields the coagulation rate $Q$:

$$Q = \frac{4}{3} \frac{\partial v_{L,3}}{\partial x_2} c_{2,\infty} \int_{0}^{R} x_2 \sqrt{R^2 - x_2^2} dx_2 = \frac{4}{3} R^3 c_{2,\infty} \frac{\partial v_{L,3}}{\partial x_2}$$

where the fluid velocity gradient $\frac{\partial v_{L,3}}{\partial x_2}$ is the same as the shear rate $E_{23}$ in Eqn. 3.60 and the radius $R$ equals the radius $a_1 + a_2$ of the collision surface.
Figure 3.6: Illustration of the method using slices as applied by Smoluchowski for orthokinetic coagulation in a simple shear flow.

Part B

Camp and Stein (1943) transformed the equation derived by Smoluchowski (1917) for a simple shear flow (Eqn. 3.61) into one for turbulent flow by simply replacing the fluid velocity gradient $\frac{\partial u_2}{\partial x_2}$ with $(\frac{\varepsilon}{\nu})^{1/2}$ for the turbulent rate of strain:

$$Q = \frac{4}{3} (a_1 + a_2)^2 \sqrt{\frac{\varepsilon}{\nu}} c_{2,\infty}$$ (3.62)

It is clear that this is only a qualitative way to describe orthokinetic coagulation in a turbulent flow field.

Part C

Saffman and Turner (1956) made a slightly better estimate for orthokinetic coagulation in a turbulent flow field. They made the same assumptions as Smoluchowski (1917) (see part A of this section). For the rate of coagulation $Q$ they wrote $2\pi R^2 |w_2|$ where $w_2$ is the radial relative velocity along the radius parallel to the $x$-axis. Since $R$ is small compared to the Kolmogorov microscale, $\lambda_K$, $|w_2| = R \left| \frac{\partial v_L}{\partial x} \right|$ where $v_L$ is the $x$-component of the velocity. Furthermore, the mean square of the fluid velocity gradient for isotropic turbulence is related to $\varepsilon$ and $\nu$ through the expression $\left( \frac{\partial v_L}{\partial x} \right)^2 = \frac{4 \varepsilon}{15 \nu}$ (Taylor, 1935). Assuming that $\frac{\partial v_L}{\partial x}$ is normally distributed, we obtain $|\frac{\partial v_L}{\partial x}| = \sqrt{\frac{2 \varepsilon}{15 \nu}}$. Hence the orthokinetic coagulation
rate for turbulent flow becomes:

\[ Q = \sqrt{\frac{8\pi}{15}} (a_1 + a_2)^3 \sqrt{\frac{\epsilon}{\nu}} c_{2,\infty} \]  

(3.63)

**Part D**

We can try to improve the previous results for orthokinetic coagulation by taking into account the structure of the extensional flow field given by Eqn. 3.15. Again, the mobility function \( A \) is assumed to be 0 and hence the particle concentration is \( c_{2,\infty} \) everywhere and particle trajectories may cross the collision surface which leads to coagulation. Using Eqn. 3.46 and integrating in the region where \( v_r \) is directed towards the central particle we obtain for the orthokinetic coagulation rate:

\[ Q = \frac{4\pi\sqrt{3}}{9} (a_1 + a_2)^3 E_{33} c_{2,\infty} = \frac{14\pi}{27\sqrt{3}} S(a_1 + a_2)^3 \sqrt{\frac{\epsilon}{\nu}} c_{2,\infty} \]  

(3.64)

where Eqn. 3.14 has been used for the mean rate of extension of vortex lines \( E_{33} \). The factor is now 0.437 which is factor of three smaller than the Camp and Stein (Eqn. 3.62) and Saffman and Turner (Eqn. 3.63) expressions in parts B and C of this section. However, this expression is expected to be the most appropriate one for a turbulent flow field since the structure of the extensional flow field is properly accounted for.

**Part E**

In a turbulent flow colloidal particles are usually much smaller than the Kolmogorov microscale of turbulence \( \lambda_K \) (Eqn. 3.5) and also their interactions occur at distances much smaller than \( \lambda_K \). For this reason Levich (1962) argued that the particles are transferred by isotropic turbulence. Hence, colloidal particles contained in turbulent eddies move through the bulk liquid in a chaotic fashion and their movement is similar to that of Brownian motion. The eddy motion of particles, therefore, may be characterized by a certain turbulent diffusion coefficient \( D_t \) at scalles smaller than \( \lambda_K \). The turbulent diffusion coefficient can be estimated as:

\[ D_t \sim v_r \nu = \alpha \sqrt{\frac{\epsilon}{\nu}} \nu^2 \]  

(3.65)

where \( v_r \) is the relative particle velocity and \( \alpha \) is a constant of proportionality.

Because of the concept of turbulent diffusivity the orthokinetic coagulation can be modeled by considering only term \( \frac{4}{3} \) of the convection-diffusion equation:

\[ \frac{\partial}{\partial r} \left( r^2 D_t \frac{\partial c_2}{\partial r} \right) = 0 \]  

(3.66)
with boundary conditions \( c_2 = 0 \) for \( r = a_1 + a_2 \) and \( c_2 = c_{2,\infty} \) for \( r \to \infty \). When also continuity of \( c_2 \) over the surface \( r = \lambda_K \) is imposed, the solution for the rate of coagulation is found to be:

\[
Q = \frac{12\pi\alpha(a_1 + a_2)^3 \sqrt{\frac{e}{v}} c_{2,\infty}}{1 + \frac{2}{7}(a_1 + a_2)^3 \frac{\lambda_K}{\lambda}} \tag{3.67}
\]

which is approximately equal to:

\[
Q = 12\pi\alpha(a_1 + a_2)^3 \sqrt{\frac{e}{v}} c_{2,\infty} \tag{3.68}
\]

### Part F

Gruy and Saint-Raymond (1997) used the terms \([3]\) and \([4]\) of the convection-diffusion equation as starting point. Substituting Eqn. 3.19 for the colloidal particle velocity \( v_{r,\text{int}} \), the convection-diffusion equation reads:

\[
\frac{\partial}{\partial r} \left( r^2 \left[ \frac{D_{12}^-}{k_B T} \frac{\partial \psi}{\partial r} c_2 - \frac{D_{12}^+}{k_B T} \frac{\partial c_2}{\partial r} \right] \right) = 0 \tag{3.69}
\]

To include particle transport due to turbulent fluid flow Gruy and Saint-Raymond wanted to apply the turbulent diffusivity concept by Levich (1962) that was discussed in part E of this section. However, they simply replaced the Brownian diffusion coefficient \( D_{12}^\infty \) by the turbulent diffusivity \( D_t \) given by Eqn. 3.65. It is obvious that this is incorrect; the underlying mechanisms of particle transport were confused. This will be discussed later-on in section 4.1 which presents a novel simplified model employing turbulent diffusivity for the particle transport due to turbulent fluid flow.

### 3.5.3 Peri- and orthokinetic coagulation

#### Part A

When the Péclet number is intermediate there is a both a peri- and an orthokinetic contribution to the coagulation rate. Now use of the flow number \( Fl \) (Eqn. 3.49) makes sense. Swift and Friedlander (1964) in their study concluded that these contributions are linearly independent and therefore additive.

For the periokinetic contribution they used Brownian diffusion with colloidal particle interaction but without viscous particle interactions according to Eqns. 3.56 and 3.57. For the orthokinetic contribution they used the Smoluchowski equation for simple shear flow (Eqn. 3.61). Hence, the total rate of coagulation is given by:

\[
Q = \frac{4\pi D_{12}^\infty (a_1 + a_2) c_{2,\infty}}{W} + \frac{4}{3} (a_1 + a_2)^3 c_{2,\infty} E_{23} \tag{3.70}
\]
Part B

Van de Ven and Mason (1977b) considered all three particle transport mechanisms (terms \[2\], \[3\] and \[4\] in the convection-diffusion equation). Viscous particle interactions were taken into account (so the hydrodynamic interaction function \(G(r, \lambda)\) differs from 1) and a simple shear flow with hydrodynamic particle interaction due to fluid squeezing according to Eqn. 3.12 was considered. This implies that attractive colloidal forces are present so \(\tilde{H} a > 0\). Van de Ven and Mason suggested an expansion of \(c_2\) for the short and long distances in terms of \(\sqrt{Pe}\) to obtain an approximate solution to the convection-diffusion equation. Using the following expansion:

\[
c_2 = c_{2,0} + \sqrt{Pe} c_{2,1} + \ldots
\]  

they arrived at the following expression for the coagulation rate:

\[
Q = \frac{4\pi D_{12}^c (a_1 + a_2) c_{2,\infty}}{W} \left(1 + \frac{0.2568\sqrt{Pe}}{W} + \ldots\right)
\]  

This solution is however valid only for small \(Pe\) numbers and therefore it applies to perikinetic coagulation with a small orthokinetic contribution. We notice that the additivity property suggested in the previous part of this section by Swift and Friedlander (1964) does not hold.

Part C

The case of orthokinetic coagulation with a small perikinetic contribution was investigated by Peke and Schowalter (1983, 1985). Similar to part B of this section the terms \[2\], \[3\] and \[4\] of the convection-diffusion equation were taken into account. They used an expansion of \(c_2\) for the short and long distances in terms of \(Pe^{-1}\) and found numerical solutions to the zeroth and first perturbation equations obtained from the convection-diffusion equation. The resulting coagulation rate \(Q\) is given by:

\[
Q = Q_0 + Pe^{-1} Q_1 + \ldots
\]  

where \(Q_0\) is the coagulation rate due to orthokinetic coagulation only and \(Q_1\) is the first correction due to Brownian diffusion. An interesting point in their numerical results is that \(Q_1\) can be positive or negative depending on the value of the flow number \(Fl\) given by Eqn. 3.49. This shows that the presence of Brownian diffusion in a system undergoing orthokinetic coagulation can increase or decrease the coagulation rate depending on the importance of the viscous flow. Again, we see that the additivity of peri- and orthokinetic coagulation suggested by Eqn. 3.70 is not valid.
Part D

Zeichner and Schowalter (1977) used a trajectory analysis to study the stability of colloidal dispersions in flow fields. A simple shear flow as well as an extensional flow field were considered (term $[2]$ in Eqn. 3.34) in addition to colloidal particle interaction (term $[3]$). Particle transport due to Brownian diffusion was taken into account separately by application of the additivity assumption. Their results indicate that the exponent of the shear rate term for orthokinetic coagulation differs from 1. For a simple shear flow (Eqn. 3.60) an exponent of 0.77, and for an extensional flow field (Eqn. 3.64) an exponent of 0.86 describes the behaviour at high Péclet numbers in a better way. Van de Ven and Mason (1977a) also performed a trajectory analysis for a simple shear flow and found an exponent of the shear rate of 0.82. The difference with the result of Zeichner and Schowalter is that their exponent was determined under conditions when there are negligible repulsive colloidal interaction forces.

Part E

Zinenko and Davis (1994a,b) calculated numerically the collision rates for spherical drops of $1 - 10$ micron size at arbitrary Péclet numbers ($Pe \geq O(10^2)$). Only attractive van der Waals colloidal forces were taken into account. The coagulation of the drops was induced by gravity or due to a shear flow. The main conclusion of relevance for this work is that Brownian diffusion in the tangential direction is in most cases negligible.

Part F

The model by Pnueli et al. (1991) properly takes into account the extensional flow on the scale of the coagulating particles in a turbulent flow field as proposed by Batchelor (1980). It describes particle aggregation in the limit when one of the particles is much larger than the other one and consequently the hydrodynamic interaction is only caused by the larger particle. They showed that for orthokinetic coagulation the rate of coagulation proposed by Saffman and Turner (see Eqn. 3.63 in part C of section 3.5.2) should be multiplied with an efficiency factor equal to $7.5\left(\frac{a_1}{a_2}\right)^2$, where $a_1$ is the radius of the larger particle. When the Péclet number is of order unity, Pnueli et al. suggest (like Swift and Friedlander in part A of this section) the superposition of independently calculated peri- and orthokinetic rates of coagulation.
3.6 Two-dimensional model for arbitrary Péclet numbers

We are interested in describing the rate of coagulation for situations where all mechanisms causing particle motion can be relevant. The model should therefore be complete with a minimum of underlying simplifications that should all be justified. We employ also a usual practice to neglect the terms in the governing equation that are much smaller than the others.

For a turbulent flow field an extensional flow field (Eqn. 3.15) is most realistic (Batchelor, 1980). Because of this axisymmetry the particle flux $N_\phi$ in the azimuthal direction (terms 7 and 8 in Eqn. 3.34) vanishes. Brownian diffusion in the radial direction (term 4) is taken into account while in the tangential direction (term 6) it is neglected compared to convective motion (term 5). This is justified when in Eqn. 3.34 the term $|\nu \partial_\phi|\alpha$ is much larger than the term $|\nu \gamma \partial_\phi|\alpha$. This is most plausible when $Pe > 1$. Note that for the purpose of investigating the behaviour of the Brownian diffusion coefficient in the tangential direction ($D_\theta$) in Fig. 3.7 the hydrodynamic interaction function $H$ as a function of the dimensionless surface-to-surface distance $h$ for equal-sized particles is depicted.

![Figure 3.7: The hydrodynamic interaction function $H$ for equal-sized particles as a function of the dimensionless surface-to-surface distance $h$.](image)

*notice that in the case of no convective motion ($Pe \ll 1$) we have spherical symmetry and hence there is also no Brownian diffusion in the tangential direction.
The negligibility of tangential diffusion is furthermore supported by the findings of Zinchenko and Davis (1994a,b) (see part E of section 3.5.3) for the case of drop coalescence. Their results indicate that tangential diffusion contributes to the aggregation rate by 2—3% only in the case of small Pe and becomes completely negligible for Pe exceeding 5.

Consequently, we obtain the following convection-diffusion equation governing the distribution of particles around the central one, i.e. the particle concentration $c_2(r, \theta)$:

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \left( (v_r + v_{r,\text{int}}) c_2 - D_r \frac{\partial c_2}{\partial r} \right) \right] + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} \left( v_\theta c_2 \sin \theta \right) = 0 \quad (3.74)$$

The boundary conditions are $c_2 = 0$ at $r = a_1 + a_2$ and $c_2 = c_{2,\infty}$ when $r \to \infty$. Refer to Fig. 3.1 for a sketch of the situation considered. The first boundary condition states that when the moving particle touches the central one they immediately coagulate and form a bigger one so the probability of finding the moving particle becomes zero. The second boundary condition means that bulk conditions prevail when the two particles are at infinite separation.

This second-order partial differential equation is integrated to give $c_2(r, \theta)$. Subsequently, the radial particle flux $N_r$ is integrated with the help of Eqn. 3.46. Due to axial symmetry Eqn. 3.46 can be written in simplified form to give:

$$Q = 4\pi \int_0^{\pi/2} r^2 \sin \theta \left[ (v_r + v_{r,\text{int}}) c_2 - D_r \frac{\partial c_2}{\partial r} \right]_{r=a_1+a_2} d\theta \quad (3.75)$$

for the rate of coagulation $Q$.

### 3.7 Results obtained with the two-dimensional model

The two-dimensional convection-diffusion equation (Eqn. 3.74) given in section 3.6 was solved numerically for equal-sized particles as a function of the Péclet number for various values of the surface (zeta) potential, ionic strength, and particle size (Melis et al., 1999). This corresponds to different colloidal stabilities (expressed by the stability ratio $W$, Eqn. 3.59) and thicknesses of the electrical double layers (expressed in dimensionless form as $\kappa a$, where the Debye-Hückel constant $\kappa$ is given by Eqn. 3.31). The Péclet number (Eqn. 3.38) was varied by choosing different values for the extension rate $E$. Although the model can account for heterocoagulation, simulation results are shown mainly for equal-sized particles (homocoagulation), since the essential features of aggregating systems already become well evident from these.

With the help of Eqn. 3.75 the aggregation rate constant $Q$ is calculated and is compared
to the predictions of the limiting and simplified models that were discussed in the previous sections. Moreover, the data obtained for these cases will be used in the next chapter as a comparison to the predictions of novel simplified models for aggregation.

For all cases constant values of the following quantities were used: dimensionless Hamaker constant $H_a = 1.58$ (which corresponds to the case of polystyrene particles in aqueous solution), fluid viscosity $\mu = 10^{-3}$ Pa s, fluid density $\rho = 10^3$ kg m$^{-3}$, relative permittivity of water $\varepsilon_r = 78$, and absolute temperature $T = 298$ K. For all cases the surface potential of both particles was the same. When not explicitly mentioned, the radii of both particles were 100 nm, so $a = 100$ nm.

The algorithm developed to solve Eqn. 3.71 consists of a first step where the equation is solved along the radial direction at the tangential position $\theta = \frac{\pi}{2}$. Looking at Eqn. 3.15 we see that at that position the particle velocity in the tangential direction $v_\theta$ vanishes. Hence, the partial differential equation reduces to an ordinary, second-order differential equation:

$$\frac{1}{r^2} \frac{d}{dr} \left\{ r^2 \left[ \left( v_{r,\text{int}} - \frac{E}{2} (1 - A) r \right) c_2 - D_r \frac{dc_2}{dr} \right] \right\} = -\frac{3}{2} E (1 - B) c_2 \quad (3.76)$$

which is solved by discretizing in the radial direction using central finite differences and solving the resulting system of linear algebraic equations with the help of the routine DLSARB (IMSL Fortran Numerical Libraries). Notice that the integration field is divided into two subdomains, one very narrow ($2 < \xi < 3$ $^8$ close to the collision surface where colloidal interaction forces are significant and where the discretization grid is rather fine (that is, $\Delta \xi = 5 \cdot 10^{-1}$), and the other one for the remaining part of the domain, where a coarser discretization grid is used (that is, $\Delta \xi = 1 \cdot 10^{-2}$).

The obtained solution provides the initial condition for the second step which consists in integrating Eqn. 3.74 in the tangential direction. In this case, the Gear method (routine DIVPAG, IMSL Fortran Numerical Libraries) is used. Convergence of the algorithm is verified using an integral criterion, that is, verifying that the computed radial particle flux (Eqn. 3.75) through various surfaces enclosing the reference particle is constant.

With respect to the application of the boundary conditions, a maximum separation of 15 to 30 times the reference particle radius has been considered. In addition, equiprobability of the pair probability function (that is, $c_2 = c_{2,\infty}$) was imposed only in the part of the boundary where the flux is incoming (upstream), while the remaining part of the boundary (downstream) is treated as an open one, that is, imposing continuity of the pair

$^8\xi$ is the dimensionless center-to-center distance $\frac{r}{a}$
probability function $c_2$ and the particle flux $Q$ across the boundary.

A final remark concerns the limitations of the numerical algorithm, which exhibits convergence difficulties for values of the Debye-Hückel constant $\kappa$ larger than $5 \cdot 10^8 \text{ m}^{-1}$. For this case, the double layer forces act over an extremely short range and, therefore, the discretization procedure fails.

Table 3.1 provides an overview of the conditions of all two-dimensional model simulations in terms of the repulsion number $R_p$ (Eqn. 3.47), $\kappa \alpha$, the particle size(s) involved and the rates of extension $E$. Also, indicated is in which graph the simulation results are shown.

<table>
<thead>
<tr>
<th>Figure</th>
<th>repulsion number, $R_p$</th>
<th>dimensionless double layer thickness, $\kappa \alpha$</th>
<th>extension rate, $E$ (1/s)</th>
<th>particle sizes</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.8</td>
<td>0.27</td>
<td>33</td>
<td>$1 \cdot 10^3$</td>
<td>$a = \alpha = 100 \text{ nm}$</td>
</tr>
<tr>
<td>3.9</td>
<td>2.39</td>
<td>10.4</td>
<td>idem</td>
<td>idem</td>
</tr>
<tr>
<td>3.12</td>
<td>2.39</td>
<td>4.7</td>
<td>$1 \cdot 10^3$</td>
<td>$a = \alpha = 100 \text{ nm}$</td>
</tr>
<tr>
<td>3.13</td>
<td>2.39</td>
<td>10.4</td>
<td>idem</td>
<td>idem</td>
</tr>
<tr>
<td>3.14</td>
<td>1.53</td>
<td>1.2</td>
<td>$1 \cdot 10^3$</td>
<td>$a = \alpha = 100 \text{ nm}$</td>
</tr>
<tr>
<td>3.15</td>
<td>2.39</td>
<td>33</td>
<td>idem</td>
<td>idem</td>
</tr>
<tr>
<td>3.16</td>
<td>2.39</td>
<td>1.04 $\cdot 10^{-3}$</td>
<td>$4.4 \cdot 10^{-3}$</td>
<td>$0, 2000, 5000$</td>
</tr>
<tr>
<td>3.18</td>
<td>2.87</td>
<td>1.04 $\cdot 10^{-3}$</td>
<td>$1 \cdot 10^3, 3 \cdot 10^3, 1 \cdot 10^4, 5 \cdot 10^4$</td>
<td>$a = 200 \text{ nm}; \ a = 40 \text{ nm}$</td>
</tr>
<tr>
<td>3.19</td>
<td>2.87</td>
<td>33</td>
<td>idem</td>
<td>idem</td>
</tr>
</tbody>
</table>

Table 3.1: Overview of all two-dimensional model simulations performed.

The first case refers to unstable conditions. The repulsion number $R_p$ is equal to $0.27$ and $\kappa \alpha = 33.0$ which corresponds to a stability ratio $W$ of 1.88. Fig. 3.8 shows the calculated aggregation rate as a function of the rate of extension. For low rates of extension the aggregation rate approaches the perikinetic limit, given by Eqns. 3.58 and 3.59. On the other hand, in the limit of large $E$-values, $Q$ varies nonlinearly with $E$, thus in disagreement with the expressions given in the section on orthokinetic coagulation. To be more precise, fitting the calculated aggregation rate in the limit of large $E$-values shows that $Q$ becomes proportional to $E^{0.86}$. This is in agreement with the findings of Zeitner and Schowalter (1977) who performed a trajectory analysis (see part D of section 3.5.3). For intermediate Péclet numbers superposition of the peri- and orthokinetic contributions (the dashed line in Fig. 3.8) proposed by Swift and Friedlander (1964) (see part A of section 3.5.3) deviates from the calculated values. However, when instead the fitted aggregation rate in the limit of large $E$-values is used for the orthokinetic contribution, the predictions
Figure 3.8: Rate of coagulation $Q$ as a function of the rate of extension $E$ calculated by the two-dimensional model ($\Delta \Delta$) for an unstable case ($Rp = 0.27$, $\kappa a = 33$) and comparison to the superposition of perikinetic and orthokinetic (---: proportional to $E$; ---: proportional to $E^{0.86}$) contributions.

are improved (the continuous line in Fig. 3.8). As will be shown in the next paragraph, the additivity assumption is limited to fast aggregating systems.

The next case considers a more stable system, that is, with larger electrostatic repulsion forces ($Rp = 2.39$). The dimensionless Debye-Hückel constant $\kappa a$ is equal to 10.4 so using Eqn. 3.59 we find that $W$ for this case is 2233. The calculated results for the aggregation rate are depicted in Fig. 3.9. The aggregation rate versus $E$ curve now exhibits a sigmoidal shape but has the same limiting behaviour as in the previous case. However, application of the additivity of the peri- and orthokinetic contributions to this system fails completely as is seen from the continuous line in Fig. 3.9. The conclusion is that for slowly aggregating systems, the diffusive and the convective aggregation mechanisms interact with each other, and, therefore, the additivity assumption is not valid. But in any case for extreme values of the extension rate the coagulation rate is properly described by the respective expressions.
**Figure 3.9:** Rate of coagulation $Q$ as a function of the rate of extension $E$ calculated by the two-dimensional model (□□) for a stable case ($R_p = 2.39, \kappa a = 10.4$) and comparison to the superposition of perikinetin and orthokinetic (—: proportional to $E^{0.86}$) contributions.

In Fig. 3.10 radial profiles of the calculated particle concentration $c_2$ (or pair probability function) for the more stable case are shown at three different tangential positions ($\theta = \pi/6, \pi/3$, and $\pi/2$). There is an overshoot at all tangential positions, that is, the pair probability close to the reference particle becomes larger than that at infinite distance. This happens because the particles move more slowly than the fluid when they are close to each other.

**Figure 3.10:** Radial profiles of the particle concentration at various tangential positions for a stable latex dispersion ($R_p = 2.39, \kappa a = 10.4$) at a rate of extension $E$ of 2000 $s^{-1}$. 
In what follows we will investigate the effect of the thickness of the electrical double layer. The repulsion number is kept the same as in the previous case ($R_p = 2.39$). The thickness of the electrical double layer can be varied by changing the ionic strength of the continuous phase (see Eqn. 3.31). The dimensionless profiles of the potential energy of interaction for values of $\kappa a$ of 4.7, 10.4, and 33.0 are shown in Fig. 3.11.

![Figure 3.11: Dimensionless potential energy of interaction $\Psi(\tau)/k_B T$ as a function of the dimensionless surface-to-surface distance $h_2 = \frac{2r}{a_1 + a_2} - 2$ for various values of the dimensionless double layer thickness (I: $\kappa a = 4.7$, II: $\kappa a = 10.4$, III: $\kappa a = 33$), for all cases $R_p = 2.39$.](image)

It is observed that a decrease of the ionic strength shifts the maximum of the potential energy of interaction curve towards larger interparticle separations, but also increases its magnitude. For a stagnant fluid (periKinetic coagulation) this simply implies an increase of the stability ratio $W$, and hence a decrease of the coagulation rate $Q$. In Fig. 3.12 the corresponding simulation results of the coagulation rate as a function of the extension rate are shown (notice that this graph includes the results already shown in Fig. 3.9).

The predicted behaviour for small values of $E$ is as expected. However, at larger values of the extension rate we observe that a smaller ionic strength leads to a higher rate of coagulation, which is the reversed behaviour. This can be qualitatively justified by realizing what we remarked about the potential energy of interaction in Fig. 3.11.
Figure 3.12: The rate of coagulation $Q$ as a function of the extension rate $E$ for various values of the dimensionless double layer thickness (I: $\kappa a = 4.7$, II: $\kappa a = 10.4$, III: $\kappa a = 33$), for all cases $R\rho = 2.39$.

Although the maximum of the potential energy of interaction increases for smaller $\kappa a$-values, the probability to surpass it under the influence of fluid motion increases since the relative particle velocity is higher at larger separations (see Eqn. 3.15). Finally, at very high $E$-values, ionic strength does not play any role, since the velocity induced by colloidal interaction forces becomes negligible with respect to that induced by the bulk fluid motion. And indeed, all curves in Fig. 3.12 approach the same asymptote.

The discussion above leads to the conclusion that, at least for the conditions investigated in this work, the aggregation rate is more strongly affected by fluid motion in the case of thick double layers, that is, for low values of the ionic strength.

This is further demonstrated in Fig. 3.13 where the aggregation rates for three different operating conditions are compared as a function of the particle Péclet number (Eqn. 3.38). Different values of both ionic strength (corresponding to $\kappa a = 1.2, 10.4$, and $44.0$) and surface potential (corresponding to $R\rho = 1.53, 2.39$, and $4.25$) were selected in order to obtain for each case the same value of the stability ratio $W = 2233$, but different values of the electrical double layer thickness. For case II, a significant deviation from pure perikinetic aggregation occurs when the Péclet number equals 2, corresponding to
an approximate fivefold increase of the aggregation rate \( Q \). On the other hand, for case III at the same \( Pe \) value, the aggregation rate increases only by a factor of two and we have to increase the Péclet number up to 6 in order to have a comparable fivefold increase of the aggregation rate constant. For case I, fluid motion has a very strong effect, so that at \( Pe = 2 \), the aggregation is already close to the limiting orthokinetic mechanism. Under these conditions, the aggregation rate is 300 times larger than the value corresponding to perikinetic aggregation.

**Figure 3.13:** The rate of coagulation as a function of the particle Péclet number for three cases with different double layer thicknesses but the same stability ratio \( W = 2233 \) (I: \( R_p = 1.53, \kappa a = 1.2 \); II: \( R_p = 2.39, \kappa a = 10.4 \); III: \( R_p = 4.25, \kappa a = 44 \)).

The behaviour of the aggregation rate constant as a function of the particle size for various values of the extension rate is now considered (note that both particles have the same size).

The case of a thick electrical double layer \( (\frac{R_p}{a} = 2.39 \cdot 10^7 \text{ m}^{-1}, \kappa = 1.04 \cdot 10^8 \text{ m}^{-1}) \) is illustrated in Fig. 3.14, where the simulation results for \( E = 0, 2000, \) and 5000 s\(^{-1}\) are shown.

The aggregation rate decreases as particle size increases in the case of moderate rates of extension. On the other hand, at larger extension rates, the curves exhibit a minimum which shifts towards smaller values of particle radii at larger values of the extension rate. This behaviour can be explained by considering that the potential energy of repulsion in-
creases for larger particle sizes, thus making aggregation less likely. This effect dominates for low rates of extension, and, in fact, in Fig. 3.14, the value of $Q$ decreases continuously as particle size increases. However, for larger values of the extension rate, the convective mechanism of aggregation becomes more important, in particular for large particles. As can be seen in Fig. 3.14, for sufficiently large particle sizes, the aggregation rate increases with particle size, and this occurs the sooner the larger the value of $E$. We can consider the particle size where this reversal occurs as a critical particle size. This corresponds to a minimum in the curve of $Q$ versus $E$. For example, in the case of $E = 5000 \text{ s}^{-1}$, the critical particle size is about 50 nm.

Beyond the critical particle size, particle coagulation is favoured for larger particles.

![Figure 3.14: The rate of homocoagulation as a function of the particle size for a latex dispersion with a thick double layer at various values of the rate of extension (I: $E = 0$, II: $E = 2000 \text{ s}^{-1}$, III: $E = 5000 \text{ s}^{-1}$), for all cases $\frac{R_p}{a} = 2.39 \cdot 10^7 \text{ m}^{-1}$ and $\kappa = 1.04 \cdot 10^8 \text{ m}^{-1}$.](image)

However, since the aggregation of particles with thin double layers is only slightly sensitive to fluid motion, it follows that the curves in Fig. 3.15 ($\frac{R_p}{a} = 4.25 \cdot 10^7 \text{ m}^{-1}, \kappa = 4.4 \cdot 10^8 \text{ m}^{-1}$) exhibit a monotonously decreasing behaviour.
Finally, in Fig. 3.16 the rate of coagulation \( Q \) is shown for the case of unequal-sized particles with a size ratio \( \lambda \) equal to 0.2. Although in general the behaviour is similar to that of equal-sized particles, the rate of coagulation in the limit of large \( E \)-values for this size ratio appears to be proportional to \( E^{0.76} \) instead of \( E^{0.86} \) for equal-sized particles. The reason is that the hydrodynamic interaction functions accounting for fluid squeezing depend on the size ratio \( \lambda \). This will be demonstrated more clearly in the next chapter in section 4.2.2 where the two-dimensional model results will be compared to the results from simplified models.
Figure 3.16: The coagulation rate $Q$ as a function of the extension rate $E$ for unequal-sized particles with size ratio $\lambda = 0.2$ (oo: $Rp = 2.87$, $\kappa a = 10.4$; ++: $Rp = 5.1$, $\kappa a = 33$), for all cases $a_1 = 200$ nm.
Chapter 4

Development of simplified models for aggregation

The intention of this chapter is to develop a simplified model for aggregation which reduces the computational effort to solve the two-dimensional partial differential equation given by Eqn. 3.74, but yields similar results. Of course the simplified model must contain a description of all relevant particle transport mechanisms. The performance of the simplified models can be tested by comparing to the simulation results given in section 3.7.

The keyword for development of such a simplified model for aggregation is averaging. We can take the ensemble average of Eqn. 3.31 which is an average over many realizations. According to the ergodic theorem this is equivalent to averaging over a long period of time \( \tau_{av} \). The time of averaging must be much longer than the Lagrangian time microscale \( \tau_L \), given by Eqn. 3.35. This yields an ordinary, second-order differential equation for the averaged particle concentration \( \bar{c}_2(r) \):

\[
\frac{1}{r^2} \frac{d}{dr} \left( r^2 \left[ v_{r,int} \bar{c}_2 + \bar{v}_r \bar{c}_2 - D_r \frac{d \bar{c}_2}{dr} \right] \right) = 0
\]

There is no dependence of the particle concentration on the tangential and azimuthal direction anymore. The reason is that there is no reason for any tangential or azimuthal concentration gradients in isotropic turbulence. The radial gradient of the particle concentration results from aggregation, which is caused by colloidal forces that act in the radial direction. In other words, the netto average (steady-state) particle flux can only occur in the direction of aggregation in the system which is otherwise uniform. The three different particle transport mechanisms are easily recognized. Note that the colloidal contribution to the particle flux is simply the product of \( v_{r,int} \) (given by Eqn. 3.19) and the averaged particle concentration \( \bar{c}_2 \), since contrary to the particle concentration \( c_2 \), \( v_{r,int} \) does not exhibit fluctuations. Similar to Eqn. 3.74 the boundary conditions that need to be imposed are \( \bar{c}_2 = 0 \) for \( r = a_1 + a_2 \) (collision surface) and \( \bar{c}_2 = c_2,\infty \) for \( r \to \infty \).
This differential equation forms the framework for the development of novel simplified models. Notice that taking the ensemble average removes several terms from Eqn. 3.34, but instead of a single variable $c_2$, two new variables, namely $\overline{c_2}$ and $\overline{v_r c_2}$, appear in the governing differential equation. This is the reason why the system is unclosed and closure expressions for the contribution to the particle flux by the turbulent flow field $\overline{v_r c_2}$ need to be formulated.

4.1 Turbulent diffusion model

Since the colloidal particles are contained in turbulent eddies the fluid flow around a particle and the resulting (relative) particle velocity $v_r$ are affected by turbulent fluctuations of small scale. Hence, when the local frame of reference is attached to the particle the average particle velocity $\overline{v_r}$ is equal to zero. Notice that $v_r = \overline{v_r} + v'_r$ because of Reynolds decomposition (the same applies to the concentration $c_2$). Consequently, the turbulent transfer term $\overline{v_r c_2}$ can also be expressed as $\overline{v'_r c_2}$ employing the familiar form to describe the turbulent transport.

A closure expression for this term can be formulated using the concept of gradient diffusion yielding:

$$\overline{v'_r c_2} = -D_t \frac{dc_2}{dr} \tag{4.2}$$

where $D_t$ is the turbulent diffusivity. Levich (1962) applied this concept to orthokinetic coagulation (see part E of section 3.5.2). An important underlying aspect is that each single turbulent eddy is anisotropic. However, because of vortex stretching continuously new eddies are generated that have a smaller size. As a consequence there is a large collection of vortices in all directions and therefore we can assume that in a statistical sense the turbulent fluid is locally isotropic, although single eddies are not.

The coagulation model employing gradient turbulent diffusion as closure is based on two important assumptions.

First, particle transport is always down the gradient of $\overline{c_2}$. This selectiveness of particle transport is no problem in case of just van der Waals attractive forces (no, or weak electrostatic repulsive forces) since under such conditions no overshoot is observed in the profile of $c_2$ in the radial direction. The conclusion is that for strong electrostatic repulsive forces care must be taken when applying closure by turbulent diffusion because there is an overshoot.

Second, it is assumed that the movement of two considered particles is random. However, in fact no randomness is observed when a particular pair of particles within the
same turbulent eddy is considered. Fortunately, when a large number of particle pairs are considered that are randomly oriented in the turbulent flow field then this assumption is fulfilled (see Hinze, 1975). Notice also that the elongational flow field increases the average distance between particles but at the same time brings some of them together.

Considering the expression for the radial particle velocity $v_r$ (Eqn. 3.15) we see that the expression for the turbulent diffusivity $D_t$ at a scale smaller than the Kolmogorov microscale should have the following form:

$$D_t \sim v_r r \sim (1 - A)E r^2 = \alpha(1 - A)\sqrt{\nu r^2}$$  \hspace{1cm} (4.3)

where $\alpha$ is a constant of proportionality and the extension rate $E$ is given by Eqn. 3.14. A proper value for $\alpha$ will be estimated later-on with the help of the resulting expression for the rate of coagulation.

Substituting the closure expression (Eqn. 4.2 together with Eqn. 4.3 for $D_t$) for $v'_r v'_r$ and Eqn. 3.19 for the colloidal velocity $v_{r,\text{init}}$ in Eqn. 4.1, with a small rearrangement yields:

$$\frac{d}{dr} \left\{ r^2 \left[ (D_r + D_t) \frac{d\bar{c}_2}{dr} + \left( \frac{D_r}{k_B T} \frac{d\bar{v}^2}{dr} \right) \bar{c}_2 \right] \right\} = 0$$  \hspace{1cm} (4.4)

We can integrate once and write:

$$\left( D_r + D_t \right) \frac{d\bar{c}_2}{dr} + \left( \frac{D_r}{k_B T} \frac{d\bar{v}^2}{dr} \right) \bar{c}_2 = \frac{Q}{4\pi r^2}$$  \hspace{1cm} (4.5)

where $Q$ is the steady-state particle flux towards the central one. Before completing the solution of this differential equation for the aggregation rate $Q$ we can predict some of its characteristics when Eqn. 4.5 is rewritten as:

$$\frac{d\bar{c}_2}{dr} + \left( \frac{1}{R_D} \frac{d\bar{v}^2}{dr} \right) \bar{c}_2 = \frac{Q}{4\pi r^2(D_r + D_t)}$$  \hspace{1cm} (4.6)

In this equation $R_D$ is the diffusivity ratio $\frac{D_t}{D_r}$. Thus, utilizing Eqn. 4.3 for the turbulent diffusivity $D_t$, we obtain:

$$R_D = 1 + \frac{D_t}{D_r} = 1 + \alpha \frac{(1 - A) r^2}{G} Pe \frac{4\lambda}{(1 + \lambda)^2}$$  \hspace{1cm} (4.7)

where the particle Péclet number $Pe$ is defined as in Eqn. 3.38:

$$Pe = \frac{(e/\nu)^{1/2} a^2}{D}$$

The ratio $\frac{(1 - A) G}{G}$ for size ratios $\lambda$ between 0 and 1 ranges between 0 and 2. The behaviour of $\frac{(1 - A)}{G}$ is discussed in more detail in appendix C with the help of literature data and the
expressions for $G(r,\lambda)$ and $A(r,\lambda)$ presented in appendix A and B, respectively. For this reason, for small $Pe$ ($Pe \to 0$), or better to say for $(\alpha (1-A) r^2 \gamma (1+\lambda)^2)^{-1} \gg Pe$, the influence of turbulent mixing is negligible ($R_D \approx 1$). On the other hand, when $D_t \gg D_r$ (turbulent diffusion controlling) the DLVO term $\frac{1}{k_BT} \frac{d\phi}{dr} c_2$ in Eqn. 4.6 is multiplied by $\frac{D_r}{D_t}$. This implies that Brownian diffusion effects can only be neglected completely when attractive and repulsive forces can be neglected as well. In other words, when turbulent diffusion is controlling, the colloidal forces are to be neglected; if they cannot be neglected, the Brownian diffusion effects should be taken into account as well. Notice that this is in agreement with the remark concerning Eqn. 3.19 that for both Brownian diffusion and velocity induced by colloidal interaction the same mechanism of friction between the particles and the surrounding fluid occurs.

Realizing that Eqn. 4.6 is an ordinary, first order, nonhomogeneous differential equation the analytical solution can easily be found:

$$Q = 4\pi D_{12}^\infty (a_1 + a_2) c_{2,\infty} \left( a_1 + a_2 \right) \int_0^\infty \frac{e^{-1} R_D k_BT \frac{d\phi}{dr} dr'}{R_D G(r,\lambda) r^2} dr'$$

The denominator is similar to the stability ratio given by Eqn. 3.59 for perikineti coagulation, but now includes the contribution by turbulent diffusion. Of course, these two expressions are identical when the diffusivity ratio $R_D$ is equal to 1.

Let us now consider the case when turbulent diffusion dominates ($R_D \gg 1$), so colloidal interaction and hence automatically Brownian diffusion are neglected. When viscous particle interactions are also neglected (i.e. both the ratio $\frac{(1-A)}{G}$ and $G$ are equal to 1) another simplified coagulation case is reached. In this case the turbulent diffusivity $D_t$ scales as:

$$D_t \sim \sqrt{\frac{\epsilon}{\nu}} r^2$$

Substitution in the general solution obtained for $Q$ (Eqn. 4.8) yields:

$$Q \sim 4\pi c_{2,\infty} \sqrt{\frac{\epsilon}{\nu}} \left( \int_{a_1+a_2}^\infty r^{-1} dr \right)^3 \sim 4\pi (a_1 + a_2)^3 \sqrt{\frac{\epsilon}{\nu}} c_{2,\infty}$$

which is nothing else but a relation similar to the ones given in the section on orthokinetic coagulation in a turbulent flow field such as the expression obtained by Saffman and Turner (1956) in part C of section 3.5.2. It is seen that several simplifying assumptions need to be made to arrive at this result.
The importance of attractive colloidal forces can be shown by having a closer look at Eqn. 4.8. For high Péclet numbers and neglecting colloidal interaction, the denominator scales as:

\[ \int_{a_1 + \sigma}^{\infty} \frac{dr}{(1 - A(r, \lambda))r^4} \]  

(4.11)

which approaches infinity since \( A(r, \lambda) \rightarrow 1 \) for \( r \rightarrow a_1 + \sigma \). This shows that attractive colloidal forces are required for coagulation to occur (unless the hydrodynamic interactions between the particles are completely removed).

We can now make an estimate for the constant of proportionality \( \alpha \) in Eqn. 4.3 for the turbulent diffusivity \( D_t \). This can be done in different ways.

In the first method we compare the result obtained by Saffman and Turner (1956) (see Eqn. 3.63 in part C of section 3.5.2) with Eqn. 4.10. In this way we find that the constant of proportionality \( \alpha \) is equal to \( \frac{\nu}{12} \approx 0.0343 \).

Another possibility, again putting the mobility function \( A \) equal to 0, is to calculate the convective flux with the help of the velocity profile given by Eqn. 3.15. This was already done in part D of the section on orthokinetic coagulation and the result for the coagulation rate \( Q \) is Eqn. 3.64. Comparison with the limiting expression of the turbulent diffusion model Eqn. 4.10 yields a value of 0.0116 for the constant of proportionality \( \alpha \). This value was used here because the particle velocity profile is taken into account more properly.

The predictions of the turbulent diffusion simplified model will now be compared to simulation results of the two-dimensional model given in section 3.7.

We will first consider unstable conditions. In Fig. 4.1 we see that there is considerable agreement between the two-dimensional model and the turbulent diffusion model. This could be be expected since with unstable conditions the profile of the particle concentration in the radial direction does not show a significant overshoot (see Fig. 4.2). In the limit of large extension rates, the rate of coagulation becomes linearly proportional to \( E \) although according to the results from the two-dimensional model this should be proportional to \( E^{0.86} \) for equal-sized particles.

However, for more stable conditions the results deviate strongly for intermediate values of the extension rate as can be seen in Fig. 4.3. The explanation is that particle transport down the gradient does not comply with the observed overshoot in the radial profile of the particle concentration already shown in Fig. 3.10.

Despite the restriction to unstable conditions we notice that this simplified model prop-
Figure 4.1: Results of the turbulent diffusion model (—) compared to the two-dimensional model results (△△) for an unstable latex dispersion ($R_p = 0.27$, $\kappa a = 33$).

Figure 4.2: Radial profiles of the particle concentration at various tangential positions for an unstable latex dispersion ($R_p = 0.27$, $\kappa a = 33$) at a rate of extension $E$ of 2000 s$^{-1}$. 
erly applies closure by turbulent diffusion for the turbulent transfer term \( \overline{v_r c_2} \) in Eqn. 4.1 and is complete. Both statements illustrate once more the contrast with the simplified model (Eqn. 3.69) proposed by Gruy and Saint-Raymond (1997) in part F of section 3.5.2. The turbulent particle transport gives rise to an additional term in the convection-diffusion equation (Eqn. 4.1) which should not be multiplied by the hydrodynamic interaction function for Brownian diffusion of particles.

Notice that besides turbulent diffusion there exist alternative closure possibilities for the term \( \overline{v_r c_2} \) such as second-order closure. Moreover, instead of employing a turbulent diffusivity \( D_t \) proportional to \( v_r r \) (according to Eqn. 4.3) one can also use \( v_r^2 \tau_S \) in which \( \tau_S \) is the strain rate correlation time, which we can assume to be equal to the Lagrangian time microscale given by Eqn. 3.35.

### 4.2 Convective motion model employing two zones

The intention of this section is to develop a simplified model which gives improved predictions of the coagulation rate for more stable systems. When the Lagrangian time microscale \( \tau_L \) (Eqn. 3.35) is much longer than the characteristic time of elongation \( \tau_E \) the
extensional flow is persisting, which means that the flow field has a stable character during a "long" period of time $\tau_L$. As discussed in section 3.4 this requirement translates into a Reynolds number, $Re_L$, which has to be larger than 60. As we know this condition is satisfied for a turbulent flow field and therefore the steady-state relative particle velocity profile given by Eqn. 3.15 can be employed.

As visualized in Fig. 4.4, a surface fraction $X_A$ of the collector surface is inflow (upstream) region, and the remaining fraction $(1 - X_A)$ outflow (downstream) region. Denoting the upstream and downstream regions by the indices "1" and "2", respectively, and averaging around the whole particle, we can write the following balance equation for the particle flux $N_r$ in the radial direction:

$$N_r = (\overline{v_r}c_2)_1X_A + (\overline{v_r}c_2)_2(1 - X_A) + v_{r,\text{ini}}c_2 - D_r \frac{dc_2}{dr} \tag{4.12}$$

where $(\overline{v_r}c_2)_i$ for $i = 1, 2$ are the convective fluxes in the two regions. The rate of coagulation $Q$ is evaluated as $4\pi r^2 N_r$ because averaging was performed around the whole particle.

In this context $\overline{c_2}$ is a weighted average:

$$\overline{c_2} = X_A\overline{c_{2,1}} + (1 - X_A)\overline{c_{2,2}} \tag{4.13}$$

where $\overline{c_{2,i}}(r)$ is the average particle concentration in region $i$ at a radial position $r$. The usual boundary conditions are imposed for $\overline{c_{2,i}}$, that is, $\overline{c_{2,1}} = 0$ at $r = a_1 + a_2$ and
We see that in Eqn. 4.12, besides the particle concentrations $c_{2,i}$, two additional variables appear, namely the convective fluxes $(\overline{\nabla r_{i}c_{2}})_{i}$ for $i = 1, 2$. At first sight this is a disadvantage, however it allows us to introduce more information about the structure of the flow field in the solution.

To reduce the number of variables $(\overline{\nabla r_{i}c_{2}})_{i}$ is expressed as:

$$
(\overline{\nabla r_{i}c_{2}})_{i} = \rho_{i}\overline{\nabla r_{i}c_{2,i}}
$$

(4.14)

where $\overline{\nabla r_{i}d}$ are the averaged radial particle velocities in the two regions. $\rho_{i}$ represent correction factors which take into account the profile of the particle concentration in the tangential direction. As an example Fig. 4.5 shows some profiles of the particle concentration in the tangential direction at various radial positions for a stable latex dispersion. Generally, $\rho_{i}$ can be a function of geometry $(\lambda, r)$ and process conditions. Although hypothetical, first we assume a limiting value of unity for $\rho_{i}$, realizing that not taking into account the dependence of the particle concentration on the tangential position may cause model deviations.

Figure 4.5: Profile of the particle concentration in the tangential direction at various radial positions for a stable latex dispersion $(R_{p} = 2.39, \kappa a = 10.4)$ at an extension rate $E$ of $2000\ s^{-1}$ obtained from the two-dimensional model.

With the help of the expressions describing the extensional flow field (Eqn. 3.15) the
averaged radial velocities in the upstream and downstream region read:

\[
\bar{v}_{r,1} = -\frac{1}{3} E(1 - A)r \\
\bar{v}_{r,2} = \frac{1}{6} (\sqrt{3} + 1) E(1 - A)r
\]

Employing Eqn. 4.14 for the convective fluxes \((\bar{v}_r \bar{c}_2)_i\), and using \(X_A = \frac{1}{\sqrt{A}}\) for the surface fraction occupied by the inflow region, transforms Eqn. 4.12 into:

\[
-\frac{1}{9} \sqrt{3} E(1 - A) r (\bar{c}_{2,1} - \bar{c}_{2,2}) + \bar{v}_{r, \text{init}} \bar{c}_2 - D_r \frac{d\bar{c}_2}{dr} = \frac{Q}{4\pi r^2}
\]

The first term on the left-hand side represents exchange by convection between the inflow and outflow region. From Eqn. 4.13 we find that \(\bar{c}_{2,1} - \bar{c}_{2,2} = \frac{c_2 - c_{2,\infty}}{X_A}\) but still we need an additional equation to solve the governing equation for \(\bar{c}_2\) and determine the coagulation rate \(Q\).

One possibility is to employ the following differential equation for the downstream region, obtained by averaging Eqn. 3.74 in the tangential direction from \(\theta = 0\) until \(\theta_{cr}\):

\[
\frac{1}{r^2} \frac{d}{dr} \left\{ r^2 \left[ (\bar{v}_{r,2} + \bar{v}_{r, \text{init}}) \bar{c}_{2,2} - D_r \frac{d\bar{c}_{2,2}}{dr} \right] \right\} = \frac{1}{2} (\sqrt{3} + 1) E(1 - B) \bar{c}_{2,1}
\]

Notice that the term describing the exchange by convection between the inflow and outflow region contains \(\bar{c}_{2,1}\) which is the tangentially averaged particle concentration in the upstream region, in agreement with \(\rho_1 = 1\). This also reflects in one of the boundary conditions for \(\bar{c}_{2,2}\): when \(r \to \infty\), \(\bar{c}_{2,2} \to \bar{c}_{2,1} \to c_{2,\infty}\). However, in reality the fluid on the boundary between the two regions has a particle concentration \(c_2(r, \theta_{cr})\) whereas this simplified model assumes that it is \(\bar{c}_{2,1}\).

The system of differential equations consisting of Eqn. 4.17 for the whole particle and Eqn. 4.18 for the downstream region is solved, yielding directly the rate of coagulation \(Q\). Fig. 4.6 shows a comparison between this simplified model and the results obtained from the two-dimensional model for an unstable and for a stable latex dispersion. As we have seen in the previous section there is disagreement with the results from the two-dimensional model (see section 3.7) for stable latex dispersions (see Fig. 4.3) when turbulent diffusion is used as closure for the term \(\bar{v}_r \bar{c}_2\). However, we observe that the simplified model proposed here yields improved agreement with the results for a stable latex dispersion.
Figure 4.6: Results of the two zones model (---) compared to the two-dimensional model for a stable latex dispersion (□□: $R_p = 2.39$, $\kappa\theta = 10.4$) and for an unstable latex dispersion (△△: $R_p = 0.27$, $\kappa\theta = 33$).

To achieve a better picture of the profile of the particle concentration $c_2$ in the tangential direction we can employ a presumed concentration profile. For the modeling of a turbulent reacting flow Tryggvason and Dahn (1991) used a similar method for molecular mixing and chemical reaction in strained laminar diffusion layers. As a basis for the presumed concentration profile we can make use of the results obtained with the two-dimensional model in section 3.7, in particular the tangential profiles of $c_2$ at various radial positions shown in Fig. 4.5 for a stable latex dispersion.

As a basis for the presumed profile we express the particle concentration $c_2$ in terms of $\sin\theta$. This choice is in line with the shape of the two-dimensional convection-diffusion equation (Eqn. 3.74) and of the extensional flow field (Eqn. 3.15). However, we should keep in mind that any monotonic function $f(\theta)$ can be used instead of $\sin\theta$.

Using a linear profile for $c_2(r, \theta)$ in the range from $\theta_{cr}$ up to $\frac{\pi}{2}$ (inflow region):

$$c_2(r, \theta) = a \cdot \sin\theta + b \quad (4.19)$$

where both $a$ and $b$ are functions of the radial position $r$. The profile should be such that $c_2(r, \theta)$ equals $c_2(r, \theta_{cr})$ on the boundary between the inflow and the outflow region.
(θ = θ_{cr}), and \( c_2(r, \frac{\pi}{2}) \) for \( \theta = \frac{\pi}{2} \). Hence, for the functions \( a(r) \) and \( b(r) \) we get:

\[
\begin{align*}
a(r) &= \frac{c_2(r, \frac{\pi}{2}) - c_2(r, \theta_{cr})}{1 - \sin \theta_{cr}} \\
b(r) &= c_2(r, \theta_{cr}) - a(r)
\end{align*}
\]  

(4.20) (4.21)

Alternatively, instead of using a linear profile in the inflow region we can take a parabolic profile \( c_2(r, \theta) = a \cdot \sin^2 \theta + b \cdot \sin \theta \). Similarly, the functions \( a \) and \( b \) depend on the radial position \( r \) and guarantee the correct values of \( c_2(r, \theta) \) for \( \theta = \theta_{cr} \) and \( \theta = \frac{\pi}{2} \).

In the remaining part from 0 up to \( \theta_{cr} \) (outflow region) there are again several options for the presumed profile of \( c_2(r, \theta) \):

1. We can use a constant value for \( c_2(r, \theta) \) equal to \( c_2(r, \theta_{cr}) \).

2. Similar to the inflow region we can use a linear profile in terms of \( \sin \theta \) and we assume that the intersect for \( \theta = 0 \) is 0. Hence, \( c_2(r, \theta) = d \cdot \sin \theta \) where the function \( d \) depends on the radial position \( r \) and is given by:

\[
d(r) = \frac{c_2(r, \theta_{cr})}{\sin \theta_{cr}}
\]

(4.22)

such that \( c_2(r, \theta) \) equals \( c_2(r, \theta_{cr}) \) for \( \theta = \theta_{cr} \).

Since the second option proposed for the downstream region does not satisfy the symmetry feature of the solution, i.e. \( \frac{\partial c_2}{\partial \theta} = 0 \) at \( \theta = 0 \), only a constant value equal to \( c_2(r, \theta_{cr}) \) was used in the downstream region.

The procedure to calculate the coagulation rate \( Q \) with the help of a presumed concentration profile in the tangential direction is as follows.

The first step is to obtain the radial profile of the particle concentration at \( \theta = \frac{\pi}{2} \). This is done by solving Eqn. 3.76 with the usual boundary conditions \( c_2(r, \frac{\pi}{2}) = 0 \) at \( r = a_1 + a_2 \) and \( c_2(r, \frac{\pi}{2}) = c_2,\infty \) when \( r \to \infty \).

Subsequently, the presumed concentration profile is inserted into Eqn. 3.74 which is then averaged in the tangential direction from \( \theta = 0 \) up to \( \frac{\pi}{2} \). This yields an ordinary, second-order differential equation for \( c_2(r, \theta_{cr}) \), the particle concentration at \( \theta = \theta_{cr} \). The specific form of this differential equation depends on the choice made for the presumed concentration profile in the tangential direction.

Finally, the coagulation rate \( Q \) is found by integrating the obtained particle concentration profile with the help of Eqn. 3.75. In Fig. 4.7 the results predicted by this simplified model...
are compared to the results obtained from the two-dimensional model. Similar to the previous simplified model, where no tangential dependence of the particle concentrations within the different zones was used, there is good agreement for both the unstable and the stable latex dispersion. In fact, the deviation for the stable latex dispersion is smaller when a presumed concentration in the tangential direction is used. Moreover, similar to the results obtained from the two-dimensional model, the simplified model results indicate that the rate of coagulation in the limit of large $E$-values is proportional to $E^{0.86}$.

\[ \text{Figure 4.7: Results of the two zones model with a presumed concentration profile in the tangential direction (---) compared to the two-dimensional model for a stable latex dispersion (□□: $R_P = 2.39$, $\kappa a = 10.4$) and for an unstable latex dispersion (△△: $R_P = 0.27$, $\kappa a = 33$).} \]

Figs. 4.8 and 4.9 show a comparison between the particle concentration profile in the tangential direction obtained from the two-dimensional model and the presumed one that was used in the simplified model. As expected, the particle concentrations at $\theta = \frac{\pi}{2}$ are the same. However, we see that the concentration profile derived from the simplified model is lower than that obtained from the two-dimensional model for most tangential positions, but always higher close to $\theta = 0$. Notice that the simulations with the two-dimensional model did not take into account Brownian diffusion in the tangential direction. In combination with the open boundary condition imposed for $r \to \infty$ in the downstream region, there is no possibility in the two-dimensional model to have particle concentrations differing from 0 for $\theta = 0$. On the other hand, the ordinary differential equation for the particle concentration at $\theta = \theta_{cr}$ in the simplified model is obtained by averaging of Eqn.
3.74 in the tangential direction from $\theta = 0$ up to $\frac{\pi}{2}$. As a result, the particle concentration at $\theta = 0$ is not zero and this could be thought of as a way to account for the Brownian diffusion in the tangential direction neglected in the two-dimensional model.

Figure 4.8: Profiles of the particle concentration in the tangential direction at various radial positions for a stable latex dispersion ($R_p = 2.39$, $\kappa\alpha = 10.4$) at an extension rate $E$ of $2000\ s^{-1}$ obtained from the two-dimensional model (---) and comparison to the presumed profiles (symbols).

Figure 4.9: Profiles of the particle concentration in the tangential direction at various radial positions for an unstable latex dispersion ($R_p = 0.27$, $\kappa\alpha = 33$) at an extension rate of $2000\ s^{-1}$ obtained from the two-dimensional model (---) and comparison to the presumed profiles (symbols).
4.2.1 Characteristics derived from the convective motion model

In this section some characteristics of the distribution of the particles around the central particle will be discussed. For this purpose we make use of Eqn. 4.12. In particular the overshoot observed in the radial profile of particle concentration in Fig. 3.10 will be qualitatively explained.

For the case without aggregation and without colloidal interaction forces we obtain:

\[
(\bar{v}_r c_1^2)X_A - D_r \frac{d\bar{v}_r c_1^2}{dr}X_A + (\bar{v}_r c_2^2)2(1 - X_A) - D_r \frac{d\bar{v}_r c_2^2}{dr}(1 - X_A) = 0
\] (4.23)

When the two particles are far apart, the gradients of all averaged particle concentrations are zero. For this reason we can write:

\[
(\bar{v}_r c_2^2)2 = -\frac{X_A}{(1 - X_A)}(\bar{v}_r c_2^2)1 \approx -1.37(\bar{v}_r c_2^2)1
\] (4.24)

which shows that the (absolute) value of the convective flux in the downstream region is larger than in the upstream region.

When the two particles come closer together the mobility functions \(A(r, \lambda)\) and \(B(r, \lambda)\) start to deviate from 0 which means that the particles slow down compared to the fluid. The consequence is that the local particle concentration increases so that gradients of the particle concentration can be observed even in the absence of colloidal interaction forces.

Since the resulting Brownian diffusion of particles can only smooth the existing particle concentration profiles, the hierarchy of the \(|(\bar{v}_r c_2^2)|\)-values remains the same.

When colloidal interaction forces are operative the balance equation (Eqn. 4.12) for the whole particle needs to be considered. Due to repulsion forces \(v_{r, \text{int}} > 0\), so it is expected that \(|(\bar{v}_r c_2^2)|\) increases and \((\bar{v}_r c_2^2)2\) decreases. Since the repulsion forces do not affect the particle velocity \(v_r\), we expect \(c_2^1 > c_2^2\) in the region of repulsion. With this, the occurrence of an overshoot in the profile of particle concentration in the radial direction has been made plausible.

4.2.2 Comparison for unequal-sized particles

The simplified model employing two zones and a presumed concentration profile in the tangential direction was used to predict the rates of coagulation for unequal-sized particles obtained from the two-dimensional model (see Fig. 3.16). The comparison in Fig. 4.10 shows that also for unequal-sized particles the simplified model is in close agreement with the two-dimensional model. Note that in the limit of large rates of extension the two-dimensional model indicates that for equal-sized particles the coagulation rate becomes
proportional to $E^{0.86}$ (see section 3.7). However, for unequal-sized particles the exponent of $E$ in this limit appears to be 0.76 instead. The explanation for this different exponent is that the hydrodynamic interaction functions for unequal-sized particles differ from those for equal-sized particles (see appendices A and B).

Figure 4.10: Results of the two zones model (—) compared to the two-dimensional model for unequal-sized particles with size ratio $\lambda = 0.2$ (oo: $R_p = 2.87$, $\kappa a = 10.4$; ++: $R_p = 5.1$, $\kappa a = 33$), for all cases $a_1 = 200 \, nm$. 
Chapter 5

Experimental validation of the model

5.1 Introduction

The intention of this chapter is to validate the predictions of the population balance equation in the perikinetiic limit with the help of coagulation experiments under different conditions and using different latex dispersions. These latex dispersions are well-defined and have been characterized in different ways in particular concerning their initial size and surface coverage with emulsifier during the coagulation experiments. All experiments are carried out below the critical micelle concentration. Coagulation is induced by the addition of a salt solution to the initial latex dispersions. Limited stirring is applied to guarantee homogeneity with respect to the salt concentration in the coagulating dispersion. The evolution of the particle size distribution is followed by means of dynamic light-scattering. Comparison of the experimental data for the average particle size to the model predictions enables formulation of a model for the counterion adsorptivity as a function of operating conditions. The predictions of the PBE reveal the formation of a multimodal particle size distribution in the course of a coagulation experiment and indicate areas where both the coagulation model and the experimental technique can be improved.

5.2 Experimental procedure

5.2.1 Preparation of polystyrene latex dispersions

As previously mentioned, to validate the predictions of the population balance equation incorporating the perikinetiic coagulation model, coagulation experiments under different conditions were carried out using spent latex dispersions (so-called seed). The word "spent" indicates that no polymerization is taking place and that residual monomer was completely removed. Such experiments need considerable amounts of different latex dis-
persions, possibly with a narrow particle size distribution. These seeds were prepared by emulsion polymerization (see for instance Gilbert, 1995). A typical polymerization recipe is shown in Table 5.1.

<table>
<thead>
<tr>
<th>double distilled water</th>
<th>938 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>monomer styrene</td>
<td>200 g</td>
</tr>
<tr>
<td>initiator sodium persulfate</td>
<td>1 g</td>
</tr>
<tr>
<td>emulsifier sodium dodecylsulfate (SDS)</td>
<td>10 g</td>
</tr>
<tr>
<td>stirring rate</td>
<td>400 rpm</td>
</tr>
<tr>
<td>temperature</td>
<td>60 °C</td>
</tr>
</tbody>
</table>

**Table 5.1:** Typical recipe for preparation of latex seeds by emulsion polymerization.

Styrene was chosen as monomer since in the literature on coagulation a polystyrene latex dispersion is often used as a model system. To avoid additional complications, the only cations occurring in the emulsion polymerization are (monovalent) sodium ions, referring to the same cations from the salt (NaCl) used to destabilize the latex dispersions during the coagulation experiments. In the course of the polymerization the monomer conversion was monitored by IR gravimetry, as described in section 5.3.1. When the degree of monomer conversion does not change further, some hydroquinone inhibitor (in solid form) was added to eliminate any residual radical activity in the latex dispersion. Moreover, the residual monomer is removed by stripping with nitrogen. Notice that the small accompanying loss of water is negligible.

<table>
<thead>
<tr>
<th>index</th>
<th>average particle diameter, nm</th>
<th>weight fraction of solids, 100 wt %</th>
<th>g SDS used</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>71</td>
<td>17.05</td>
<td>10</td>
</tr>
<tr>
<td>B</td>
<td>75</td>
<td>16.31</td>
<td>7.5</td>
</tr>
<tr>
<td>C</td>
<td>76</td>
<td>16.58</td>
<td>7.5</td>
</tr>
<tr>
<td>D</td>
<td>74</td>
<td>15.81</td>
<td>5</td>
</tr>
<tr>
<td>E</td>
<td>98</td>
<td>15.89</td>
<td>2</td>
</tr>
<tr>
<td>F</td>
<td>114</td>
<td>14.82</td>
<td>1.5</td>
</tr>
<tr>
<td>G</td>
<td>137</td>
<td>14.98</td>
<td>1.4</td>
</tr>
</tbody>
</table>

**Table 5.2:** Summary of the properties of the different latex seeds.

Table 5.2 summarizes the properties of the different latex dispersions which were prepared. The amounts of SDS used and the resulting average particle sizes (by dynamic light-scattering) and solid weight fractions (by IR gravimetry) are indicated. The electrolyte concentration in the continuous phase of the original latex dispersions is mainly due to residual initiator. At the considered temperature only a few percent of the initiator
are consumed during the polymerization reaction and are found in the polymer chains as a terminal group. On the other hand, during all coagulation experiments induced by the addition of NaCl, the main contribution to the electrolyte concentration is given by the added NaCl.

5.2.2 Perikinetic coagulation experiments

The initial latex dispersions, prepared according to section 5.2.1, are very stable as can be seen from the values of the stability ratios \( W \) calculated by Eqn. 3.59 at the average particle size and given in Table 5.3. The zeta potential required to calculate the stability ratio is also given and is estimated according to the results of the zeta potential measurements at various NaCl concentrations discussed in section 5.6.1. The two latex dispersions indicated with an asterix (E* and F*) were prepared by adding 0.0425 g and 0.11 g of SDS to 50 ml of the latex dispersions E and F, respectively.

<table>
<thead>
<tr>
<th>index</th>
<th>predicted zeta potential, ( \zeta ) (mV)</th>
<th>stability ratio, ( \log W )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>60.07</td>
<td>31.36</td>
</tr>
<tr>
<td>B</td>
<td>57.46</td>
<td>29.96</td>
</tr>
<tr>
<td>C</td>
<td>57.37</td>
<td>30.25</td>
</tr>
<tr>
<td>D</td>
<td>51.17</td>
<td>22.54</td>
</tr>
<tr>
<td>E</td>
<td>40.58</td>
<td>17.11</td>
</tr>
<tr>
<td>E*</td>
<td>54.31</td>
<td>34.52</td>
</tr>
<tr>
<td>F</td>
<td>39.55</td>
<td>18.58</td>
</tr>
<tr>
<td>F*</td>
<td>99.65</td>
<td>154.78</td>
</tr>
<tr>
<td>G</td>
<td>41.38</td>
<td>25.17</td>
</tr>
</tbody>
</table>

Table 5.3: Zeta potentials and stability ratios of the different latex seeds before destabilizing them by the addition of a NaCl solution.

To observe noticeable perikinetic coagulation it is necessary to increase the electrolyte concentration in the continuous phase. This is done by adding a concentrated aqueous NaCl solution (concentration \( C_{NaCl}^{add} \), volume \( V_{add} \)) to the initial latex dispersion with volume \( V_{disp} \). The resulting mixture is stirred for a short time to achieve homogeneity, in particular with respect to the NaCl concentration in the continuous phase. Since the initial latex dispersion does not contain NaCl, the resulting NaCl concentration is:

\[
C_{NaCl} = \frac{C_{NaCl}^{add} V_{add}}{x V_{disp} + V_{add}} \tag{5.1}
\]

where \( x \) is the volume fraction of continuous phase in the initial latex dispersion. Note that, for the same reason (dilution), the specific particle surface \( (S_p) \) and the number of particles per unit volume of continuous phase \( (n_p) \) decrease. The NaCl concentrations
that induce an acceptable rate of perikinetic coagulation for the different latex dispersions were chosen by trial-and-error. For all coagulation experiments 1 ml of concentrated NaCl solution was added to 5 ml of latex dispersion.

It was verified that under all experimental conditions the depth of the possible secondary minimum in the curve of the potential energy of interaction $\psi(r)$ is much smaller than $k_B T$. For this reason the coagulation in our system is taking place in the primary minimum, and therefore is irreversible.

A serious experimental problem is that the addition of a concentrated NaCl solution causes local NaCl concentrations higher than the desired value. The characteristic time for bulk fluid mixing for the system considered here was estimated with the help of acid-base decolourization experiments. The pH-indicator phenolphtalein was added to 5 ml of NaOH solution, and 1 ml HCl solution having different concentrations were added. The time needed to obtain a transparent solution (that is to say that it is neutralized or has become acidic) was measured and is proportional to the characteristic time for bulk fluid mixing. In spite of the fact that the characteristic time for bulk fluid mixing appears to be of the order of 1 second, usually it is larger than the characteristic time for coagulation $\tau_{1/2}$ (Eqn. 3.42) because the coagulation frequency $\beta$ is increased significantly by the locally higher NaCl concentration. This means that few large aggregates can form immediately after salt addition.

It is notable that this problem can be suppressed, or even avoided, when the coagulation experiments are carried out under more dilute conditions. In this case one can add a small amount of latex dispersion to a NaCl solution having a concentration only slightly higher than the desired one, and subsequent mixing for a short time to achieve homogeneity. The locally higher particle concentration ($N_{2.0}$) occurring at the beginning of the bulk fluid mixing reduces the characteristic time for coagulation $\tau_{1/2}$, but this effect is much smaller than the reduction due to a locally higher NaCl concentration. Since the investigation of particle coagulation in concentrated latex dispersions is closer to the industrial practice, all coagulation experiments were induced by the addition of a concentrated NaCl solution, thus accepting the possible initial formation of few large aggregates. Fortunately, in most cases the size of these initially formed aggregates is such that they will sediment and therefore will not disturb the actual coagulation experiment we are interested in.
5.2.3 Sampling and characterization

After the addition of the concentrated salt solution from time to time samples were taken from the coagulating latex dispersion. The samples were taken more frequently at the beginning of a coagulation experiment. Each sample was diluted with double distilled water. The dilution factor was such that both the particle concentration and the NaCl concentration are reduced significantly, and therefore the progress of coagulation becomes negligible. Moreover, the resulting particle concentration in the sample is suitable for measurement of the particle size distribution by dynamic light-scattering without further sample treatment. Typically, a sample of 30 μl was diluted with 5 ml of double distilled water. However, the sample volume remains an adjustable parameter because the scattering intensity increases with the particle size (see section 5.3.2), which in turn increases by aggregation.

<table>
<thead>
<tr>
<th>index</th>
<th>NaCl concentration in the aqueous phase, C_{NaCl} (mM)</th>
<th>ionic strength, I (mM)</th>
<th>emulsifier surface coverage, θ</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>206.86</td>
<td>218.29</td>
<td>0.5076</td>
</tr>
<tr>
<td>A2</td>
<td>229.85</td>
<td>241.28</td>
<td>0.5073</td>
</tr>
<tr>
<td>A3</td>
<td>252.83</td>
<td>264.26</td>
<td>0.5070</td>
</tr>
<tr>
<td>B1</td>
<td>171.48</td>
<td>182.77</td>
<td>0.4208</td>
</tr>
<tr>
<td>B2</td>
<td>182.91</td>
<td>194.2</td>
<td>0.4206</td>
</tr>
<tr>
<td>B3</td>
<td>205.77</td>
<td>217.07</td>
<td>0.4202</td>
</tr>
<tr>
<td>B4</td>
<td>238.64</td>
<td>239.93</td>
<td>0.4199</td>
</tr>
<tr>
<td>C1</td>
<td>171.92</td>
<td>183.20</td>
<td>0.4176</td>
</tr>
<tr>
<td>C2</td>
<td>206.3</td>
<td>217.58</td>
<td>0.4170</td>
</tr>
<tr>
<td>D1</td>
<td>125.4</td>
<td>136.52</td>
<td>0.2848</td>
</tr>
<tr>
<td>D2</td>
<td>136.8</td>
<td>147.92</td>
<td>0.2844</td>
</tr>
<tr>
<td>D3</td>
<td>148.2</td>
<td>159.32</td>
<td>0.2841</td>
</tr>
<tr>
<td>D4</td>
<td>159.6</td>
<td>170.72</td>
<td>0.2838</td>
</tr>
<tr>
<td>D5</td>
<td>170.99</td>
<td>182.12</td>
<td>0.2836</td>
</tr>
<tr>
<td>D6</td>
<td>193.79</td>
<td>204.92</td>
<td>0.2833</td>
</tr>
<tr>
<td>E1</td>
<td>160.05</td>
<td>171.04</td>
<td>0.1471</td>
</tr>
<tr>
<td>E2</td>
<td>182.92</td>
<td>193.9</td>
<td>0.1469</td>
</tr>
<tr>
<td>E3</td>
<td>205.78</td>
<td>216.77</td>
<td>0.1468</td>
</tr>
<tr>
<td>E1*</td>
<td>205.78</td>
<td>216.83</td>
<td>0.2152</td>
</tr>
<tr>
<td>E2*</td>
<td>228.64</td>
<td>239.69</td>
<td>0.2151</td>
</tr>
<tr>
<td>E3*</td>
<td>251.51</td>
<td>262.55</td>
<td>0.2150</td>
</tr>
<tr>
<td>F1</td>
<td>135.89</td>
<td>146.89</td>
<td>0.1376</td>
</tr>
<tr>
<td>F2</td>
<td>147.21</td>
<td>158.21</td>
<td>0.1374</td>
</tr>
<tr>
<td>F3</td>
<td>158.54</td>
<td>169.54</td>
<td>0.1373</td>
</tr>
<tr>
<td>F1*</td>
<td>294.42</td>
<td>305.64</td>
<td>0.3495</td>
</tr>
<tr>
<td>F2*</td>
<td>317.07</td>
<td>328.29</td>
<td>0.3494</td>
</tr>
<tr>
<td>G1</td>
<td>204.13</td>
<td>215.14</td>
<td>0.1518</td>
</tr>
<tr>
<td>G2</td>
<td>226.82</td>
<td>237.82</td>
<td>0.1517</td>
</tr>
<tr>
<td>G3</td>
<td>249.5</td>
<td>260.51</td>
<td>0.1516</td>
</tr>
</tbody>
</table>

Table 5.4: Overview of the conditions for the perikinet coagulation experiments.

Table 5.4 provides an overview of the NaCl concentrations that were used in the co-
agulation experiments with the different latex dispersions given in Table 5.2. In the table each experiment is identified by adding a number to the letter identifying the original seed. Employing the Langmuir adsorption isotherm (Eqn. 5.30 in section 5.3.5) for SDS, the emulsifier surface coverage θ was calculated for the conditions at the beginning of each coagulation experiment, i.e. immediately after the salt addition. To cover a wider range of surface coverages, the initial coverages of two seeds were artificially increased by SDS addition (runs indicated by an asterix). The results of all experiments will be discussed and compared with model predictions in section 5.5, after the presentation of all techniques used for characterization in the next section.

5.3 Techniques used for characterization

5.3.1 Gravimetry

To measure the solid content (polymer plus additives, i.e. initiator, emulsifier and salts) of a latex dispersion, the gravimetric technique was used. This can be applied to both reacting and nonreacting samples and is based on measuring the sample weight before and after complete drying. The drying process was carried out over a short time using an IR gravimetry device (HG53 Halogen Moisture Analyzer, Mettler Toledo). Notice that a small amount (much smaller than the weight of the sample) of inhibitor (hydroquinone) was mixed with the sample taken prior to starting the gravimetric analysis. This prevented continued polymerization during the thermal exposure. In combination with the recipe used for the emulsion polymerization we can easily derive useful data for the latex dispersion such as the degree of monomer conversion and the volume fraction of continuous phase.

The weight fraction of solids, wt, is given by:

\[ \text{wt} = \frac{P + E + I}{P + M + W + E + I} \tag{5.2} \]

where P stands for polymer, E for emulsifier, M for monomer, I for initiator, and W for water. Notice that only water and residual monomer evaporate during thermal exposure. For reacting systems, since we have \( M_0 = M + P \) where \( M_0 \) is the initial amount of monomer, the degree of monomer conversion \( X \) can be calculated as:

\[ X = \frac{\text{wt}(M_0 + W + E + I) - (E + I)}{M_0} \tag{5.3} \]

Alternatively, for nonreacting systems without residual monomer we can derive the ratio \((P/W)\) from Eqn. 5.2:

\[ (P/W) = \frac{\text{wt} + \frac{E + I}{W}(\text{wt} - 1)}{1 - \text{wt}} \tag{5.4} \]
Using this result we can calculate the volume fraction $x$ of continuous phase in the latex dispersion:

$$x = \frac{1}{(P/W) \frac{\rho_k}{\rho_p} + 1} \quad (5.5)$$

With the help of dynamic light-scattering measurements (see section 5.3.2) the average particle diameter $\bar{d}$ of the latex dispersion was measured (in fact we measure the hydrodynamic radius $R_h$). This enables us to calculate the number of polymer particles per unit volume of continuous phase:

$$n_p = \frac{(P/W) \frac{\rho_k}{\rho_p}}{\frac{\pi}{6} \bar{d}^3} \quad (5.6)$$

The specific particle surface $S_p$ is simply the product of $n_p$ and the surface of a single particle:

$$S_p = n_p \pi \bar{d}^2 \quad (5.7)$$

Note that only the average particle size $\bar{d}$ is used here to calculate the number of polymer particles per unit volume of continuous phase and the specific particle surface. This is a reasonable assumption at the beginning of a coagulation experiment since at that point the particle size distribution is narrow. However, the initial particle size distribution can be taken into account more accurately as will be shown in the next section.

### 5.3.2 Dynamic light-scattering (DLS)

With the help of light-scattering the average size and broadness of a sufficiently diluted sample from a particle dispersion can be measured (see Kerker, 1969; Schurtenberger and Newman, 1993; Fitch, 1997). When a light beam crosses a latex dispersion it is scattered. The particle sizes considered here (particle radii $a$ between 35 and 90 nm) are smaller than $\frac{\lambda_0}{4}$ where $\lambda_i$ is the wavelength of the incident light (660 nm). For this reason we can apply the Rayleigh-Debye theory to describe the intensity of the scattered light as a function of the angle of observation $\theta$ and parameters such as particle size and vacuum wavelength of the light ($\lambda_0$). The angular dependence of scattered light intensity results from interference of light waves from different parts of the same particle. To obtain the angular dependence of the scattering intensity, one defines the scattering vector $Q_\ast$ as:

$$Q_\ast = \frac{4\pi n_0}{\lambda_0} \sin \frac{\theta}{2} \quad (5.8)$$

where $n_0$ is the refractive index of the medium.

For a monodisperse colloidal dispersion having a number concentration $N$ of particles with
volume \( v \) the scattering intensity \( I(Q_*) \) becomes:

\[
I(Q_*) = K_* N v^2 P(Q_*, a)
\]  

(5.9)

where \( K_* \) is the Rayleigh scattering intensity of a single particle:

\[
K_* = 9\pi^2 \left( \frac{n_0}{\lambda_0} \right)^4 \left( \frac{m^2 - 1}{m^2 + 2} \right)
\]  

(5.10)

in which \( m = \frac{n}{n_0} \) is the ratio of polymer and medium refractive indices. \( P(Q_*, a) \) is the so-called \emph{form factor} which gives the dependence on particle size (\( a \)) and angle of observation as follows:

\[
P(Q_*, a) = \left( \frac{3(\sin(Q_* a) - Q_* a \cos(Q_* a))}{(Q_* a)^3} \right)^2
\]  

(5.11)

Eqn. 5.9 shows that the scattering intensity has a sixth power dependency on the particle radius. For a monodisperse dispersion a single measurement of the scattering intensity \( I(Q_*) \) suffices to calculate the particle volume \( v \) and hence the particle size.

The distribution of particle sizes in a dispersion is taken into account in Eqn. 5.9 by replacing \( N v^2 \) by \( \sum N_i v_i^2 \). To evaluate the particle size distribution, the scattering intensity \( I(Q_*) \) is measured at different angular positions. The particle size distribution \( (N_i, v_i) \) is obtained by solving the corresponding set of equations (all in the form of Eqn. 5.9) and is used to calculate average particle size and breadth of the particle size distribution. The method of light-scattering described here is called \emph{static light-scattering}.

When the spectrum of the scattered light is analyzed it is seen to be line-broadened. This comes about because of the thermal motions of the scattering particles which cause Doppler shifting of the light to higher or lower frequencies, depending upon whether the particle is moving towards or away from the detector at the \emph{moment} of observation. With the help of photon counting one can correlate the scattering intensity at various time intervals \( \tau \). Employing the variation in time of the scattering intensity is the principle of \emph{quasi-elastic light-scattering} or, more simply, \emph{dynamic light-scattering}. This yields the temporal autocorrelation function \( g(Q_*, \tau) \) which for a polydisperse system is written as:

\[
g(Q_*, \tau) = \int_0^\infty G(\Gamma) \exp(-\Gamma \tau) d\tau
\]  

(5.12)

where the weight function:

\[
G(\Gamma) = \frac{N(a) a^6 P(Q_*, a)}{\int_0^\infty N(a) a^6 P(Q_*, a) da}
\]  

(5.13)

gives the relative scattering contribution of a component with decay rate \( \Gamma = Q_*^2 D \) in which \( D \) is the \emph{diffusion coefficient} of a particle with radius \( a \) and \( N(a) \) its number concentration.
For narrow size distributions, the exponentials in Eqn. 5.12 can be expanded around an average decay rate $< \Gamma >$, which leads to:

$$
g(Q_\ast, \tau) = \exp(-< \Gamma > \tau) \left[ 1 + \frac{\sigma}{2} < \Gamma >^2 \tau^2 + \ldots \right]
$$

(5.14)

We can thus obtain an average decay rate $< \Gamma >$ and a coefficient of variation $\sigma$ from a second-order polynomial fit in $\tau$ to $\ln \{g(Q_\ast, \tau)\}$, a so-called cumulant analysis. Note that the cumulants method requires no prior knowledge about the particle size distribution. From the average decay rate, $< \Gamma >$, obtained from the initial slope of $\ln \{g(Q_\ast, \tau)\}$, we can then calculate an intensity weighted diffusion coefficient, $< D >$. From this value, using Eqn. 3.16, we can estimate the average hydrodynamic radius $R\_h$, while the polydispersity index $\sigma$ can be deduced from the second cumulant. The average hydrodynamic radius is intensity weighted which means that in terms of moments $\lambda_i$ of the particle radius distribution $F(r)$ it can be written as:

$$
R\_h = \frac{\lambda_6}{\lambda_5} = \frac{\int_{r_0}^{\infty} \tau^6 F(r) \, dr}{\int_{r_0}^{\infty} \tau^5 F(r) \, dr}
$$

(5.15)

Similarly, for the polydispersity index $\sigma$:

$$
\sigma = \frac{\lambda_4 \lambda_8}{\lambda_5^2} - 1
$$

(5.16)

As the population balance equation yields the time evolution of the particle volume distribution $f(v)$, while from the dynamic light-scattering measurements we find $R\_h$ and $\sigma$ of the samples taken in terms of the particle radius distribution $F(r)$, we need to formulate an expression relating their moments $\mu_i$ and $\lambda_i$, respectively. Both moments are given by an expression similar to Eqn. 2.9. Because spherical shape is assumed particle volume and radius are related by the monotonic expression $v = \frac{4}{3} \pi r^3$. Requiring $f(v)dv = F(r)dr$, that is, the number of particles in a volume interval $dv$ is the same as in the corresponding radius interval $dr$, we find that the relation between the moments $\mu_i$ and $\lambda_i$ is:

$$
\lambda_i = \left( \frac{3}{4\pi} \right)^{i/3} \mu_{i/3}
$$

(5.17)

Using Eqn. 5.17, the expressions for the hydrodynamic radius and polydispersity index can be rewritten as:

$$
R\_h = \left( \frac{3}{4\pi} \right)^{1/3} \frac{\mu_2}{\mu_{5/3}}
$$

(5.18)

and,

$$
\sigma = \frac{\mu_2 \mu_{4/3}}{\mu_{5/3}^2} - 1
$$

(5.19)
respectively.

For the coagulation experiments performed in this study a ZETASIZER 5000 (Malvern Instruments) was used to measure the average particle size of the samples by dynamic light-scattering.

Instead of using the cumulants method described above for illustrative purposes, the inversion of the temporal autocorrelation function \( g(Q_*, \tau) \) (given by Eqn. 5.12) was performed by means of the more robust Contin method (Provencher, 1982a,b). This method uses the prior knowledge that the simplest solution, i.e. the one that reveals the least amount of new information or detail for the distribution function, is to be preferred (parsimony principle) (see also Finsy, 1994). This is achieved by constrained regularization. Similar to the cumulants method the Contin method provides us with estimates for the intensity weighted hydrodynamic radius \( R_h \) and polydispersity index \( \sigma \).

### 5.3.3 Scanning electron microscopy (SEM)

Some images obtained from scanning electron microscopy (SEM) of latex dispersions were used to validate the measurements of particle size by dynamic light-scattering. Because polystyrene is a nonconducting material the sample surface can accumulate a static charge which distorts the electronic beam. To avoid this the surface was coated with a metallic conductor such as gold (by a shadowing-like method). The images made for several latex dispersions are shown in Fig. 5.1.
It is seen that the initial particle size distributions are reasonably narrow. Table 5.5 compares the average particle sizes measured by DLS and estimated from the SEM-images. This estimate is somewhat rough; we simply measured the particle sizes from the photograph and no more than a few tens of particles were considered. This means that the measurement is not significant from the statistical viewpoint (at least 1500 particles should be counted) but we are using it as a qualitative validation of the DLS measurements. The results in Table 5.5 indicate that DLS is a suitable technique to follow the time evolution of the average particle size at least below a certain degree of polydispersity, since the comparison was performed using the original seeds, before inducing any coagulation.
<table>
<thead>
<tr>
<th>index</th>
<th>average particle diameter by DLS (nm)</th>
<th>average particle diameter by SEM (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>71</td>
<td>≈ 69</td>
</tr>
<tr>
<td>E</td>
<td>98</td>
<td>≈ 100</td>
</tr>
<tr>
<td>G</td>
<td>137</td>
<td>≈ 140</td>
</tr>
</tbody>
</table>

Table 5.5: Comparison between the average particle diameter measured by DLS and SEM.

### 5.3.4 Zeta potential

When a colloidal particle with its surrounding electrical double layer is subjected to an external electrical field, \( \mathcal{E} \), it will tend to move with a velocity, \( v_\mathcal{E} \), towards the electrode with charge opposite to that on the particle surface (see Hunter, 1981). The electrical force exerted by the electrical field is balanced by viscous friction. For the zeta potential measurements that were performed, the dimensionless electrical double layer thickness \( \kappa a \) (cf. Eqn. 3.31 in section 3.3.2) is much larger than 1. For this case Smoluchowski (1921) related the zeta potential at the OHP (see Fig. 3.5) to the resulting electrophoretic mobility \( V_\zeta \) (defined as the particle velocity per unit of applied electrical field \( \mathcal{E} \)) through the following equation:

\[
V_\zeta = \frac{v_\mathcal{E}}{\mathcal{E}} = \frac{\kappa \zeta}{\mu}
\]  

(5.20)

where \( \epsilon \) is the permittivity of the dielectric medium and \( \mu \) is the dynamic fluid viscosity. An oscillating electrical field is applied which causes the particles to move back and forth within the measurement cell. The induced particle velocity is measured with the help of laser Doppler velocimetry and using Eqn. 5.20 the corresponding zeta potential is evaluated. The measurements of the zeta potential were also carried out with the ZETASIZER 5000 (Malvern Instruments).

In the following, a series of measurements of the zeta potential of the polymer particles in the latex dispersion as a function of the electrolyte concentration will be described. Since the number concentration of the initial latex dispersion is too high (at the particular particle size considered), the resulting count rate is higher than that suitable for accurate measurements of the particle velocity by laser Doppler velocimetry. However, dilution with double distilled water is not appropriate since this would alter the composition of the continuous phase and therefore change the value of the zeta potential. For this reason, dilution was undertaken using the serum obtained by ultrafiltration of the latex dispersion considered (see section 5.3.7).
5.3.5 Adsorption of surfactant

The polystyrene particles are stabilized using an ionic emulsifier, sodium dodecylsulfate (abbreviated SDS, \(C_{12}H_{24}HSO_4Na\)). The SDS is partitioned between the surface of the polymer particles and the aqueous (continuous) phase. The overall mass balance for SDS in the latex dispersion can therefore be written as:

\[
C_{e,\text{tot}} = C_{e,w} + S_p \gamma
\]  

(5.21)

where \(C_{e,\text{tot}}\) is the total concentration of SDS in the latex dispersion, expressed as moles per unit volume of continuous phase. The volume fraction of the continuous phase in the latex dispersion (\(x\)) is estimated from the measured weight fraction of solids in the latex dispersion (see section 5.3.1). \(C_{e,w}\) is the SDS concentration in the aqueous phase, and \(S_p\) is the specific particle surface per unit volume of continuous phase. Furthermore, \(\gamma\) is the concentration of SDS on the surface of the polymer particles (mol \(\cdot m^{-2}\)). The maximum concentration of SDS on the surface, \(\gamma_\infty\), is reached when the emulsifier concentration in the aqueous phase increases to its maximum value, i.e. its solubility in water. A surface concentration equal to \(\gamma_\infty\) corresponds to a surface coverage \(\theta\) of 1, being \(\theta\) defined as:

\[
\theta = \frac{\gamma}{\gamma_\infty}
\]  

(5.22)

Measurements of the maximum surface concentration of SDS on polystyrene polymer particles as a function of the NaCl concentration were performed by Piirma and Chen (1980) by surface tension titration curves and also from electron microscopy data. In fact, they obtained the molecular areas \(A_0\) of surfactants at saturation adsorption of these surfactants. This quantity is inversely proportional to \(\gamma_\infty\) through the following expression:

\[
\gamma_\infty = \frac{1}{A_0 N_{A_0}}
\]  

(5.23)

where \(N_{A_0}\) is the Avogadro number. The following empirical expression was used to describe \(\gamma_\infty\) as a function of \(C_{\text{NaCl}}\) in the range 0 to 100 mM:

\[
\gamma_\infty = \left(2.8368 \cdot 10^5 - \frac{7.4625 \cdot 10^4 C_{\text{NaCl}}^2}{C_{\text{NaCl}}^2 + 5.102 \cdot 10^2}\right)^{-1}
\]  

(5.24)

Fig. 5.2 depicts the dependence of \(\gamma_\infty\) on \(C_{\text{NaCl}}\) and the comparison with the data by Piirma and Chen. The electrostatic repulsion between the polar heads of the surfactant molecules is reduced due to screening by a greater concentration of \(Na^+\)-counterions and hence a higher NaCl concentration increases \(\gamma_\infty\). As we can see a plateau is reached for NaCl concentrations exceeding 100 mM.
Figure 5.2: \( \gamma_\infty \) as a function of the NaCl concentration in the aqueous phase: experimental data by Piirma and Chen (\( \gamma_\infty \)), empirical expression used here \((-\)-).

As the system during the coagulation experiments contains besides NaCl other ions (residual initiator, emulsifier present in the aqueous phase) an equivalent NaCl concentration on the basis of ionic strength (see section 3.3.2) has been used to simulate the presence of these ions.

The maximum value of the emulsifier concentration in the aqueous phase is its water solubility or critical micelle concentration, CMC. Above this value micelles are formed. Micelles are in fact aggregates of emulsifier molecules with a structure such that the polar heads of the emulsifier molecules point in the direction of the aqueous phase (see sketch in Fig. 5.3).

![micelle](image.png)

**Figure 5.3:** Possible partitioning of emulsifier molecules between the polymer particle surface (adsorbed) and the aqueous phase (free, or in the form of micellar structures).

Similar to \( \gamma_\infty \) the critical micelle concentration is a function of the electrolyte concentration in the aqueous phase. The values for the critical micelle concentration reported
by Shaw (1980) were fitted by a third-order polynomial to facilitate interpolation of the CMC-values given in the NaCl concentration range from 0 to 300 mM:

\[
CMC = \left(3.3 \cdot 10^{-2}C_{NaCl}^3 - 18.636C_{NaCl}^2 + 6971C_{NaCl} + 1.2346 \cdot 10^5\right)^{-1}
\] (5.25)

Fig. 5.4 shows the CMC as a function of the NaCl concentration and the experimental data reported by Shaw. For all latex dispersions studied here the emulsifier concentration in the aqueous phase was well below the CMC.

![Figure 5.4: Critical micelle concentration (CMC) of SDS as a function of the NaCl concentration in the aqueous phase: experimental data by Shaw (o), empirical expression used here (-).](image)

In addition to the overall mass balance Eqn. 5.21 we require one more expression to calculate the emulsifier surface coverage \( \theta \). For this purpose we employ an adsorption isotherm. There are several options, ranging from the oversimplified case of no partitioning (or complete irreversible adsorption) to a linear or a Langmuirian type adsorption isotherm. Let us briefly examine each option.

When all SDS is adsorbed on the polymer particles (i.e. no partitioning), the concentration in the aqueous phase \( C_{e,\infty} \) is 0. The resulting surface coverage follows directly
from Eqns. 5.21 and 5.22 and is:

$$\theta = \frac{C_{e,\text{tot}}}{S_{p,\text{tot}}^{\infty}}$$  \hspace{1cm} (5.26)

Due to the high affinity between polymer and SDS, along with the low solubility of the emulsifier in water, this could be a reasonable approximation for the particular case under examination.

The second option employs a linear adsorption isotherm which expresses the fact that the adsorbed concentration of the emulsifier ranges from $\theta = 0$ when no emulsifier is in the aqueous phase ($C_{e,w} = 0$) to complete coverage ($\theta = 1$) when the emulsifier concentration in the aqueous phase is equal to the CMC. Thus, the corresponding linear adsorption isotherm can be written as:

$$\theta = \frac{C_{e,w}}{C_{\text{CMC}}}$$  \hspace{1cm} (5.27)

Combination of the overall mass balance (Eqn. 5.21) with the linear adsorption isotherm for SDS yields the following expression for the SDS concentration in the aqueous phase:

$$C_{e,w} = \frac{C_{e,\text{tot}}}{1 + \frac{S_{p,\text{tot}}^{\infty}}{C_{\text{CMC}}}}$$  \hspace{1cm} (5.28)

It is seen that when the ratio $\frac{S_{p,\text{tot}}^{\infty}}{C_{\text{CMC}}} \ll 1$, most of the emulsifier is present in the aqueous phase. On the other hand, when $\frac{S_{p,\text{tot}}^{\infty}}{C_{\text{CMC}}} \gg 1$, which is typical for the system considered here, most emulsifier is adsorbed onto the polymer particles and the limiting case of no partitioning discussed above is approached.

Another SDS partitioning law considered here is a Langmuirian type adsorption isotherm. Accordingly, the following expression for the emulsifier surface coverage applies:

$$\theta = \frac{K_1 C_{e,w}}{1 + K_2 C_{e,w}}$$  \hspace{1cm} (5.29)

where $K_1$ and $K_2$ indicate the corresponding parameters. To estimate the parameters for this isotherm, the aqueous phase SDS concentration was measured at different values of the total SDS concentration in the system (employing latex dispersion B), as discussed in more detail in section 5.3.6. The resulting Langmuir adsorption isotherm is:

$$\theta = \frac{5.46758 \times 10^{-3} C_{e,w,\text{ppm}}^{\text{ppm}}}{1 + 4.6261 \times 10^{-3} C_{e,w,\text{ppm}}^{\text{ppm}}}$$  \hspace{1cm} (5.30)

where $C_{e,w,\text{ppm}}^{\text{ppm}}$ is the same as $C_{e,w}$ but with units ppm instead. The reason to use these units is that the concentrations allowed for analysis by ion chromatography are in the ppm range.
Figure 5.5: Comparison between the different emulsifier adsorption isotherms (----: linear; ---: Langmuirian) and experimental data obtained by ion chromatography (**) using latex dispersion E.

A comparison between the experimental SDS adsorption isotherm data and the three models considered (Eqns. 5.26, 5.27 and 5.30, respectively) is given in Fig. 5.5. It is obvious that the Langmuirian adsorption isotherm provides the most appropriate description.

<table>
<thead>
<tr>
<th>C_{NaCl} (mM)</th>
<th>emulsifier surface coverage $\theta$, no partitioning</th>
<th>idem, linear adsorption isotherm</th>
<th>idem, Langmuir adsorption isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.6648</td>
<td>0.5974</td>
<td>0.6448</td>
</tr>
<tr>
<td>28.73</td>
<td>0.5606</td>
<td>0.5337</td>
<td>0.5484</td>
</tr>
<tr>
<td>57.46</td>
<td>0.5337</td>
<td>0.5159</td>
<td>0.5230</td>
</tr>
<tr>
<td>114.92</td>
<td>0.5211</td>
<td>0.5096</td>
<td>0.5112</td>
</tr>
<tr>
<td>206.86</td>
<td>0.5174</td>
<td>0.5093</td>
<td>0.5076</td>
</tr>
<tr>
<td>252.83</td>
<td>0.5167</td>
<td>0.5098</td>
<td>0.5070</td>
</tr>
</tbody>
</table>

Table 5.6: Comparison between the emulsifier surface coverage calculated using the three different adsorption isotherms at three salt concentrations for a typical latex dispersion (A).

Table 5.6 shows the results of the calculation of the surface coverage of a typical latex dispersion (A) at different NaCl concentrations using the different adsorption isotherms discussed above. In general the calculated surface coverages do not differ much, although for low NaCl concentrations there is better agreement between the surface coverage calculated assuming complete adsorption and using the Langmuir isotherm. Moreover, the surface coverages at the two highest NaCl concentrations calculated, using the Langmuir
isotherm, do not differ much. The reason is that for NaCl concentrations higher than 100 mM the value of $\gamma_\infty$ does not change significantly (see Fig. 5.2). Note that for higher NaCl concentrations the surface coverages calculated using a linear adsorption isotherm and assuming complete adsorption agree better due to the reduced value of the CMC (see Fig. 5.4).

5.3.6 Ion chromatography

To determine the adsorption isotherm of SDS on polystyrene particles, ion chromatography is applied to measure the emulsifier concentration in the aqueous phase $C_{e,aw}$. Ion chromatography is a form of liquid chromatography where the stationary and the mobile phase are such that a separation between the different ions is achieved. Possible ions present in the aqueous phase besides sodium ions are dodecylsulphate, persulphate, chloride and sulphate. Here we used a Metrohm 690 Ion Chromatograph (which uses conductivity as the detection method) with as mobile phase a 55/45 mixture of methanol and water with a concentration of ammoniumacetate ($CH_3COONH_4$) of 17 mg·l$^{-1}$. The column used as stationary phase was a Nucleosil 120-5 C18.

The overall mass balance for SDS in the latex dispersion (Eqn. 5.21) allows us to evaluate the concentration of SDS ($\gamma$) on the surface of the polymer particles:

$$\gamma = \frac{C_{e, tot} - C_{e, aw}}{S_p}$$  \hspace{1cm} (5.31)

The procedure followed to measure the adsorption isotherm is to add different (known) amounts of SDS to a well-defined latex dispersion, i.e. a system whose particle size and weight fraction of solids have been evaluated before. Note that the SDS is added in solid form to avoid the volume change effects which would also affect the emulsifier equilibrium. In this way, the surface concentration $\gamma$ increases after each addition. To achieve surface concentrations lower than that of the initial seed it is possible to increase the volume of the continuous phase by adding double distilled water. In this way, the complete range of emulsifier surface concentrations can be explored and we can construct the complete SDS adsorption isotherm. An ultrafiltration unit (see section 5.3.7) is used to make the required phase separation between the continuous and the particulate phase of the latex dispersion after each addition or dilution. The filtrate is subsequently analyzed using ion chromatography.

The ultrafiltration should be done with care to avoid a shift of the emulsifier equilibrium during the filtration. For this reason, only a small amount of filtrate was collected with negligible formation of a cake of polymer particles on top of the filter. Moreover, the
Figure 5.6: Typical chromatogram obtained by ion chromatography of the continuous phase of a latex dispersion. The peak at a retention time of 6.75 min corresponds to dodecylsulphate.

...slightly hydrophilic nature of the filter material should not cause hindrance to passage of SDS, thus resulting in an apparently lower SDS concentration in the obtained filtrate. The absence of such a problem was verified by the following experiments. First we prepared a series of calibration standards with SDS concentrations in the range of interest. Letting these standards pass through the ultrafiltration unit, and afterwards measuring the SDS concentrations by ion chromatography, only a small difference of about 5% was found. It is necessary to dilute the obtained filtrates with double distilled water to reach the concentration range suitable for analysis by ion chromatography. A typical chromatogram obtained is shown in Fig. 5.6.

5.3.7 Ultrafiltration

This technique allows us to separate the continuous phase from a latex dispersion. The simplified sketch in Fig. 5.7 illustrates the technique. The phase separation is performed in batch mode. The latex dispersion is continuously stirred with a magnetic stirrer to prevent the formation of a cake of polymer particles on top of the filter. The ultrafiltration device used is a GYROSEP 75 Stirred Cell (INTERSEP). The average pore size of the filter (Filtron) is 100 kD (kiloDalton) which corresponds to about 7 nm. Hence, it is expected that a nearly complete phase separation can be achieved. An average pressure of 1.5 bar is applied to force the continuous phase of the latex dispersion through the filter material. The filter material is polyether sulphone which was found to have only small interaction with the emulsifier, as previously explained.
Figure 5.7: Sketch of the ultrafiltration device used to separate the continuous phase from a latex dispersion.

5.3.8 Soap titration

In addition to ion chromatography combined with ultrafiltration (see sections 5.3.6 and 5.3.7) another technique was applied to obtain information about the SDS adsorption isotherm on polystyrene particles. In the so-called soap titration, SDS is added to a latex dispersion and the change of a characteristic property of the latex dispersion such as conductivity or surface tension is monitored (Maron, 1954). It appears that the graphs of these properties as a function of the amount of SDS added exhibit an inflection point when the critical micelle concentration is reached. In this way the emulsifier equilibrium in the original latex dispersion can be examined by comparison of the CMC with the amount of SDS that was added. In this work the conductivity of the latex dispersion was measured. This was done with a Conductometer 660 (Metrohm). The SDS is added in solid form to avoid increase of the volume of the continuous phase which would also affect the emulsifier equilibrium. After each SDS addition the latex dispersion was stirred for about 5 minutes to be sure that the new SDS equilibrium has established. Following section 5.3.5 we can write the following balance equation for the amount of SDS to be added (expressed as the change of the total emulsifier concentration \( \Delta C_{e,\text{tot}} \)) to reach the inflection point:

\[
\Delta C_{e,\text{tot}} = S_f \gamma_\infty (1 - \theta) + CMC - C_{e,w}
\]  

(5.32)

Substituting the predicted location of the emulsifier equilibrium in the original latex dispersion (equilibrium coordinates \((C_{e,w}, \theta)\)) in this equation for \( \Delta C_{e,\text{tot}} \) and comparison to the amount added during the soap titration is a check of the reliability of the SDS adsorption isotherm used. As an example, Fig. 5.8 shows the soap titration curve obtained for latex dispersion A. The amount added \((\approx 0.39 g)\) to 50 ml of latex dispersion agrees
reasonably well with the calculated amount using Eqn. 5.32 (0.33 g) keeping in mind that it is difficult to determine the exact location of the inflection point.

![Soap titration curve obtained for latex dispersion A and determination of the inflection point.](image)

**Figure 5.8:** Soap titration curve obtained for latex dispersion A and determination of the inflection point.

### 5.4 Population balance equation model

To validate the coagulation models presented in chapters 3 and 4, using the experiments described in the previous sections, the numerical solution of the population balance equation (Eqn. 2.13) is needed to evaluate \( f(m, t) \), the time evolution of the complete number density function. Note that in the coagulation experiments spent latex dispersions were used, which means that particle volume \((v)\) and mass \((m)\) are easily related because the density of the polymer particles is constant. This implies that the experimental results for the average particle size obtained by dynamic light-scattering are compared to the ratio of moments of \( f(m, t) \) in terms of particle volume given by Eqn. 5.18. The coagulation experiments were all performed in the perikinetik limit and therefore the rate of coagulation \( \beta(v, v') \) is calculated using Eqn. 3.58 (putting \( c_{2,\infty} \) equal to 1 (as a pair distribution function, see Eqn. 3.1)), which involves the stability ratio \( W \) given by Eqn. 3.59. The zeta potential needed for the colloidal part of the coagulation model is calculated using the Stern layer model discussed in section 3.3.2. The effect of fluid squeezing on the mutual diffusion coefficient is taken into account by employing the hydrodynamic interaction function \( G(r, \lambda) \) developed in appendix A.
5.4.1 Numerical solution of the population balance equations

The population balance equations (PBEs) were solved by a relatively new numerical approach, based on a discretization technique (Kumar and Ramkrishna, 1996). This approach is the last rationalization of a large set of discretization techniques proposed in the literature to solve PBEs (e.g. Batterham et al., 1981; Houmanski et al., 1988; Landgrebe and Pratsinis, 1990). These methods are considered the most effective from the computational point of view in comparison with other numerical techniques typically used for PBEs, such as the method of weighted residuals, the method of moments, and collocation on finite elements (see Ramkrishna, 1985).

![Figure 5.9: Illustration of the discretization of the distribution \( f(v, t) \) in \( N \) classes using pivot volumes \( x_i \).](image)

In short, a discretization technique is based on replacement of the original integro-partial differential equation (Eqn. 2.13) with a set of summation-ordinary differential equations. These equations are obtained by discretization of the distribution \( f(v, t) \) in a set of \( N \) classes. Each class is identified by an "average" (or pivot) volume, \( x_i \), where \( v_i \leq x_i \leq v_{i+1} \) (see Fig. 5.9) and the corresponding number of particles is given by:

\[
N_i(t) = \int_{v_i}^{v_{i+1}} f(v, t) dv
\]  

(5.33)

With reference to a system undergoing coagulation only, integrating the original continuous PBE over a discrete size interval \( (v_i - v_{i+1}) \), the following set of equations is obtained:

\[
\frac{dN_i(t)}{dt} = \frac{1}{2} \int_{v_i}^{v_{i+1}} dv \int_{v_0}^{v_i} \beta(v - v', v') f(v - v') f(v') dv' - \int_{v_i}^{v_{i+1}} f(v, t) dv \int_{v_0}^{\infty} \beta(v, v') f(v', t) dv' - \int_{v_i}^{v_{i+1}} f(v, t) dv \int_{v_0}^{\infty} \beta(v, v') f(v', t) dv' 
\]

(5.34)

where \( i = 1 \ldots N \).

The approximate evaluation of the two integrals is obtained in terms of \( N_i(t) \) by application of the mean value theorem on frequency. For the death (or loss) term in Eqn. 5.34 this means:

\[
\int_{v_i}^{v_{i+1}} f(v, t) dv \int_{v_0}^{\infty} \beta(v, v') f(v', t) dv' \approx N_i(t) \sum_{k=1}^{M} \beta(x_i, x_k) N_k(t) 
\]

(5.35)

For the birth term, the application of the same idea introduces an additional problem since we have to define which class a particle produced by coagulation with volume \( x_i \leq v \leq x_{i+1} \)
belongs to. The key idea of the approach by Kumar and Ramkrishna is that this assignment is carried out so as to preserve two integral properties of the distribution, i.e. two moments. Typical choices are \( \mu_0 \) and \( \mu_1 \), or \( \mu_2 \) and \( \mu_1 \), depending upon the property of interest for the particular application under examination. For example, requiring preservation of overall volume and number of particles (the most common choice), the birth term becomes:

\[
\frac{1}{2} \int_{v_j}^{v_{j+1}} dv \int_{v_0}^{v} \beta(v - v', v') f(v - v', t) f(v', t) dv' \approx \]

\[
\left[ \frac{1}{2} \int_{x_i}^{x_{i+1}} a(v, x_i) dv + \frac{1}{2} \int_{x_{i-1}}^{x_i} b(v, x_i) dv \right] \int_{v_0}^{v} \beta(v - v', v') f(v - v', t) f(v', t) dv'
\]

where \( a(v, x_i) \) and \( b(v, x_i) \) define the fractions of particles formed by coagulation, which are assigned to class \( i \) and were born in the size range \((x_i - x_{i+1})\) and \((x_{i-1} - x_i)\), respectively. They are evaluated by solving the following system of equations:

\[
\begin{cases}
    a(v, x_i) + b(v, x_{i+1}) = 1 \\
    a(v, x_i)x_i + b(v, x_{i+1})x_{i+1} = v
\end{cases}
\]

which correspond to the preservation of particle number and volume. Evaluating \( a(v, x_i) \) and \( b(v, x_{i+1}) \) from these equations\(^9\) and substituting into the birth term, the following form is obtained:

\[
\sum_{j \geq k} \sum_{x_{i-1} \leq x_j + x_k \leq x_i} \left( 1 - \frac{1}{2}\delta_{j,k} \right) b(x_j + x_k, x_i) \beta(x_j, x_k) N_j(t) N_k(t) + \\
\sum_{j \geq k} \sum_{x_i \leq x_j + x_k \leq x_{i+1}} \left( 1 - \frac{1}{2}\delta_{j,k} \right) a(x_j + x_k, x_i) \beta(x_j, x_k) N_j(t) N_k(t)
\]

in which \( \delta_{j,k} \) is the Kronecker delta (\( \delta_{j,k} = 1 \) if \( j = k \), else \( \delta_{j,k} = 0 \)).

Hence, substitution of the discretized forms of the birth and death terms (Eqns. 5.38 and 5.35, respectively) into the discretized PBE (Eqn. 5.34) yields the following final form:

\[
\frac{dN_i(t)}{dt} = \sum_{j \geq k} \sum_{x_{i-1} \leq x_j + x_k \leq x_i} \left( 1 - \frac{1}{2}\delta_{j,k} \right) b(x_j + x_k, x_i) \beta(x_j, x_k) N_j(t) N_k(t) + \\
\sum_{j \geq k} \sum_{x_i \leq x_j + x_k \leq x_{i+1}} \left( 1 - \frac{1}{2}\delta_{j,k} \right) a(x_j + x_k, x_i) \beta(x_j, x_k) N_j(t) N_k(t) - \\
N_i(t) \sum_{k=1}^{M} \beta(x_i, x_k) N_k(t)
\]

\(^9\)notice that the expression for \( b(v, x_i) \) can be obtained from \( b(v, x_{i+1}) \) by cyclical exchange of the indices
This system of ordinary differential equations is solved with the help of the routine DIVPAG (IMSL Fortran Numerical Libraries).

For the population balance equation the initial particle size distribution \( f(v, t = 0) \) needs to be specified. As a model distribution, the versatile gamma distribution is used:

\[
f(v) = \frac{n_p V_{\text{cont}} \lambda}{\overline{v}(\lambda - 1)!} e^{\lambda - 1} \exp(-\lambda)
\]

where \( \lambda = \frac{\mu_p}{P_d - 1} \), \( z = \lambda v/\overline{v} \), and \( V_{\text{cont}} = x V_{\text{disp}} \) is the volume of the continuous phase in the latex dispersion with volume \( V_{\text{disp}} \). \( P_d \) stands for the polydispersity and is defined as \( \frac{\mu_{200}}{\mu_0^2} \). Since the initial distribution was always narrow \( (\sigma < 0.05) \), the polydispersity \( P_d \) was assumed to be equal to 1.05. Consequently, Eqn. 5.19 from section 5.3.2 was replaced by \( \frac{\mu_{200}}{\mu_0^2} = 1.05 \). The average particle volume \( \overline{v} \) is given by \( \frac{\mu_p}{\mu_0} \). Notice that the zeroth moment of \( f(v) \) equals \( n_p V_{\text{cont}} \) which is the total number of polymer particles in the latex dispersion. Substituting the initial hydrodynamic radius \( R_h \) measured by DLS into Eqn. 5.18 enables us to calculate the initial average particle volume \( \overline{v} \). Combining this with the measured volume fraction of solids (see section 5.3.1) yields an estimate for \( \mu_0 \).

During the solution of the population balance equation after each time step the value of the specific particle surface \( S_p \) is updated. For this purpose the moment of order \( \frac{3}{2} \) of the instantaneous particle volume distribution \( f(v, t) \) is calculated. When the value of \( S_p \) differs from the previous value by more than 1\%, the coagulation rates \( \beta(x_j, x_k) \) are recalculated.

The main advantage of the discretization technique used here is that all coagulation events are represented in a single matrix. This matrix has a limited number of elements, \( \beta(x_j, x_k) \), corresponding to the coagulation rate of the pivot volume pair \((x_j, x_k)\).

### 5.5 Comparison between experimental results and predictions from the PBE

The coagulation experiments with the different latex dispersions (Table 5.2) under the conditions summarized in Table 5.4 were carried out according to sections 5.2.2 and 5.2.3. In this section the experimental results for the time evolution of the average particle size will be compared to the predictions from the respective population balance equation. We will focus our attention to the coagulation experiments A1, A2, and A3 since the observed behaviour during the coagulation of the other latex seeds is similar. The experimental data and the numerical results from the population balance equation for these latex seeds are presented at the end of this section. Moreover, the observed behaviour will be qualita-
tively explained by investigating the time evolution of the number density function $f(v)$. When we consider the population balance equation describing the perikinetic coagulation experiments we observe that, apart from the input parameters such as initial particle size and NaCl concentration, there is only one degree of freedom which is the Langmuir constant of adsorption $K$ for the counterions. This parameter of the coagulation kernel appears to be very important regarding the stability of the latex dispersion since it determines the zeta potential value. As we have seen in section 3.3.2 the zeta potential is the key parameter for the electrostatic repulsion.

For each of the perikinetic coagulation experiments that was carried out, the value of $K$ was varied until optimal agreement was reached between the measured evolution of the average particle size and the one predicted by the population balance equation. Fig. 5.10 shows a comparison between the experimental data and the numerical results for the coagulation experiments A1, A2, and A3. Since the model employed here assumes that both coagulating particles are spherical, the comparison was made only for the initial stage of the coagulation experiments, that is, when doublet formation dominates. Hence, for the coagulation experiments with the remaining latex seeds the model predictions for the evolution of the average particle size (Figs. 5.18 to 5.25) will be shown only for the initial stage, which is about 50 minutes.

![Figure 5.10:](image)

**Figure 5.10:** Comparison between the measured (symbols) and the predicted (continuous lines) time evolution of the average particle size $d$ for the coagulation experiments A1, A2, and A3.
Table 5.7 contains the optimal values of the counterion adsorptivity as well as the corresponding zeta potential values at the beginning of these three coagulation experiments.

<table>
<thead>
<tr>
<th>index</th>
<th>counterion adsorptivity, $K \cdot 10^3$ (mM$^{-1}$)</th>
<th>zeta potential, $\zeta$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>2.2</td>
<td>43.36</td>
</tr>
<tr>
<td>A2</td>
<td>2.0</td>
<td>42.23</td>
</tr>
<tr>
<td>A3</td>
<td>1.95</td>
<td>40.44</td>
</tr>
</tbody>
</table>

Table 5.7: Optimal values of the counterion adsorptivity and the corresponding zeta potential values at the beginning of the coagulation experiments A1, A2, and A3.

It is seen that there is good agreement between the experimental data and the numerical results only at the beginning of the coagulation experiments. In fact, during the course of the coagulation experiments the predicted and measured average particle sizes start to deviate. The numerically computed average particle size reaches a plateau value while the values measured by dynamic light-scattering show a monotonic increase as time proceeds.

In terms of the size distribution, the calculated number density function $f(v, t)$ at different times are shown in Fig. 5.11 for the two coagulation experiments A1 and A3 and we can observe that the original particle size distribution becomes broader. From Table 5.4 we see that for experiment A1 coagulation is taking place at a NaCl concentration of 206.86 mM, while for A3 at 252.83 mM. It is obvious that the rate of coagulation for the latter case is higher. In Fig. 5.10 we observe that that in the course of time the rate of

![Figure 5.11: The distribution $f(v, t)$ obtained from the population balance equation for the coagulation experiments A1 (—) and A3 (oo) at two different times.](image-url)
coagulation decreases and we also find that the number density function $f(v, t)$ does not change anymore. This is explained by the fact that, due to coagulation, the specific particle surface $S_p$ decreases, and therefore the emulsifier surface coverage $\theta$ increases. Because of this, the zeta potential of the particles increases, which leads to higher stability ratios and hence lower rates of coagulation. To illustrate this, Fig. 5.12 shows the time evolution of the zeta potential of the particles having the initial size for the three cases.

![Figure 5.12](image)

**Figure 5.12:** Predicted time evolution of the zeta potential $\zeta$ of particles having the initial size for the coagulation experiments A1, A2, and A3.

In both cases the original monomodal number density function turns into a bi- or even a trimodal one. This becomes more apparent when instead of $f(v, t)$, the weighted number density function $v \cdot f(v, t)$ is plotted. The second maximum of $f(v, t)$ is found at a location corresponding to the volume of a doublet (twice the volume of a singlet). As expected, the eventual third maximum occurs at a location which corresponds to the volume of a triplet. The reason why at 206.86 $mM$ no triplets are formed is that at 206.86 $mM$ the stability ratios are larger than at 252.83 $mM$. Notice that doublets are formed by the coagulation of two singlets, and triplets by the coagulation of a doublet and a singlet. For this reason Fig. 5.13 shows the time evolution of the stability ratios $W_{11}$ and $W_{12}$, where the subscripts ”11” and ”12” refer to singlet-singlet and singlet-doublet interaction for the two cases, respectively.

Fig. 5.14 shows the predicted evolution of the polydispersity $Pd$ given by Eqn. 2.11 as $\frac{\mu_{11}}{\mu_1}$ for the coagulation experiments A1, A2, and A3. For coagulation experiment A1 the polydispersity increases monotonously and reaches a plateau value. However, for the other two coagulation experiments -especially for A3- the polydispersity first increases rapidly,
Figure 5.13: Time evolution of the stability ratios for singlet-singlet ($W_{11}$) and singlet-doublet ($W_{12}$) for the coagulation experiments A1 and A3. Reaches a maximum, and afterwards decreases until a plateau value is reached which is lower than for A1. The rapid increase is explained by the immediate formation of doublets; the decrease of the polydispersity occurs due to the fact that most of the singlets disappear, which means that an almost monomodal particle size distribution consisting mainly of doublets results. Coagulation experiment A1 does not proceed sufficiently and hence a bimodal particle size distribution remains. Coagulation experiment A2 is somewhere in between A1 and A3. To support these observations Fig. 5.15 shows the particle size distribution at $t = 400$ min for the coagulation experiments A1, A2, and A3.

Figure 5.14: Predicted time evolution of the polydispersity $Pd$ for the coagulation experiments A1, A2, and A3.
Figure 5.15: The distribution $f(v, t)$ for the coagulation experiments A1 (—), A2 (**), and A3 (o) at $t = 400 \text{ min}$.

Finally, in Figs. 5.16 and 5.17 the time evolution of the specific particle surface $S_p$ and the total number of particles $n_p V_{cont}$ (which equals the zeroth moment $\mu_0$ of $f(v, t)$) is depicted. In particular Fig. 5.16 supports the previous findings from the results of the population balance equation; as a consequence of coagulation the specific particle surface decreases which leads to higher emulsifier surface coverages and hence zeta potentials. Consequently, coagulation does not progress any further.

Figure 5.16: The predicted time evolution of the specific particle surface $S_p$ for the coagulation experiments A1, A2, and A3.
Figure 5.17: Variation in time of the total number of particles \( n_p V_{\text{cont}} \) (= \( \mu_0 \) of \( f(v, t) \)) for the coagulation experiments A1, A2, and A3 as predicted by the PBE.

Referring to the discussion in section 5.3.2 about particle radius distribution (as with DLS) and particle volume distribution (as predicted by the PBE) Table 5.8 shows a comparison between different ways to evaluate the average particle size from the PBE in terms of particle volume distribution. It is seen that the difference between the number averaged particle size \( (\mu_1^1) \), the weight averaged particle size \( (\mu_1^2) \), and the averaged particle size consistent with the DLS measurements \( (\mu_{5/3}) \) increases in the course of time.

<table>
<thead>
<tr>
<th>time</th>
<th>( \mu_1^1 ) (nm)</th>
<th>( \mu_1^2 ) (nm)</th>
<th>( \mu_{5/3} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>initially</td>
<td>69.39</td>
<td>70.53</td>
<td>70.9</td>
</tr>
<tr>
<td>50 min</td>
<td>73.48</td>
<td>75.78</td>
<td>76.6</td>
</tr>
<tr>
<td>100 min</td>
<td>74.62</td>
<td>77.09</td>
<td>77.96</td>
</tr>
<tr>
<td>200 min</td>
<td>75.8</td>
<td>78.4</td>
<td>79.3</td>
</tr>
</tbody>
</table>

Table 5.8: Comparison between different ratios of moments to evaluate the average particle size for coagulation experiment A1, initially and at \( t = 50, 100 \) and 200 minutes.

We believe that the deviation for longer times can be explained by the fact that the model inherently differs from reality. Let us briefly discuss these aspects below.

Regarding the coagulation kernel in the population balance equation, an important assumption is that all coagulating particles are assumed to behave like particles with spherical shape. For the initial, narrow particle size distributions at the beginning of the coagulation experiments this is true indeed since no coagulation has taken place yet. However, since spent latex dispersions are used, the resulting coagulated particles do not have this spherical shape anymore. Hence, the description of their Brownian diffusion as well as their
colloidal interaction should be modified and take into account the new shape. In fact, the
decrease of the specific particle surface $S_p$ is much smaller when the singlets keep their
own identity (a rigid dumbbell is formed) after coagulation has taken place. This could
be an explanation for the smaller stabilization in the course of coagulation as observed
during the coagulation experiments. Moreover, Kusters et al. (1997) demonstrate that
porous aggregates with a fractal structure have higher rates of aggregation compared to
solid particles because the fluid flow can penetrate their surface. Although in our case the
number of individual particles in an aggregate is not so high, the phenomenon described
might also play a role. Notice that for similar experiments carried out using polymer par-ticles
swollen with monomer, the spherical shape is maintained when they coagulate and
hence this inappropriate description of the coagulation process in the course of time was
not observed (Melis et al., 2000). An important modeling assumption is that only binary
particle interactions are considered. This assumption seems justified because the latex
dispersions considered are not dense (Kusters et al., 1997). In fact, because the deviations
are observed only for longer times, the occurrence of multiple encounters is probably not
an explanation.

Note that the set of $K$-values derived from the coagulation experiments indicate that the
use of a Langmuir isotherm for counterion adsorption is not appropriate. However, since
for each coagulation experiment an optimal $K$-value was used, this does not explain the
observed deviations for longer times.

Considering the experimental technique used to follow the particle size evolution, it is quite
accurate for narrow, monomodal particle size distributions while in the course of a coag-
ulation experiment the particle size distribution gets broader and becomes multimodal.
This means that the only reliable measured quantity is $R_h$ (Eqn. 5.18), i.e. some combi-
ation of strange order moments. However, since the model calculates these moments
from the whole distribution, it is believed that this also is not a possible explanation for
the found discrepancy.

In conclusion, concerning the evolution of the average particle size a meaningful com-
parison between the experimental data by DLS and the model results is only possible dur-
ing the initial period of coagulation where doublet formation dominates. This is also the
case for the remaining coagulation experiments shown in the following graphs. Typically,
the experimental data are properly described during the first 50 minutes of a coagulation
experiment.
Figure 5.18: Coagulation experiments with latex dispersion B.

Figure 5.19: Coagulation experiments with latex dispersion C.
Figure 5.20: Coagulation experiments with latex dispersion D.

Figure 5.21: Coagulation experiments with latex dispersion E.
Figure 5.22: Coagulation experiments with latex dispersion $E^*$, which is latex dispersion $E$ with additional SDS.

Figure 5.23: Coagulation experiments with latex dispersion $F$. 
Figure 5.24: Coagulation experiments with latex dispersion $F^*$, which is latex dispersion $F$ with additional SDS.

Figure 5.25: Coagulation experiments with latex dispersion $G$. 
5.6 Discussion on counterion adsorption isotherm

In Fig. 5.26 the set of optimal $K$-values under different conditions, that is, ionic strength and surface coverage at the beginning of the coagulation experiment, is displayed. Generally, a lower value of $K$ corresponds to a higher rate of coagulation. Table 5.9 contains all optimal $K$-values and the corresponding zeta potentials and stability ratios calculated using Eqn. 3.59.

![Graph showing counterion adsorption isotherm](image)

**Figure 5.26:** Optimal values of the counterion adsorption $K$ as a function of the ionic strength for all coagulation experiments that were carried out. The corresponding emulsifier surface coverages ($\theta$) are given in the legend.

Notice that the use of a single constant value of $K$ for a series of coagulation experiments at different NaCl concentrations leads to remarkable deviations as is shown in Fig. 5.27 for the coagulation experiments A1, A2 and A3. In this case the optimal value for coagulation experiment A1, that is $K = 2.2 \cdot 10^{-3} \text{mM}^{-1}$, was used to describe the coagulation experiments A2 and A3 as well.
Table 5.9: The optimal $K$-values under the different conditions of the coagulation experiments and the corresponding zeta potentials and stability ratios.

<table>
<thead>
<tr>
<th>index</th>
<th>counterion adsorptivity, $K \cdot 10^4$ (mM$^{-1}$)</th>
<th>zeta potential, $\zeta$ (mV)</th>
<th>stability ratio, $\log W$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>2.2</td>
<td>43.36</td>
<td>7.69</td>
</tr>
<tr>
<td>A2</td>
<td>2.9</td>
<td>42.23</td>
<td>6.70</td>
</tr>
<tr>
<td>A3</td>
<td>1.95</td>
<td>40.44</td>
<td>5.41</td>
</tr>
<tr>
<td>B1</td>
<td>2.57</td>
<td>42.45</td>
<td>8.06</td>
</tr>
<tr>
<td>B2</td>
<td>2.47</td>
<td>41.53</td>
<td>7.29</td>
</tr>
<tr>
<td>B3</td>
<td>2.12</td>
<td>40.89</td>
<td>6.57</td>
</tr>
<tr>
<td>B4</td>
<td>1.92</td>
<td>39.83</td>
<td>5.66</td>
</tr>
<tr>
<td>C1</td>
<td>2.67</td>
<td>41.70</td>
<td>7.11</td>
</tr>
<tr>
<td>C2</td>
<td>2.17</td>
<td>40.41</td>
<td>6.56</td>
</tr>
<tr>
<td>D1</td>
<td>3.05</td>
<td>40.41</td>
<td>7.45</td>
</tr>
<tr>
<td>D2</td>
<td>2.7</td>
<td>39.98</td>
<td>6.96</td>
</tr>
<tr>
<td>D3</td>
<td>2.42</td>
<td>39.64</td>
<td>6.56</td>
</tr>
<tr>
<td>D4</td>
<td>2.32</td>
<td>38.60</td>
<td>5.77</td>
</tr>
<tr>
<td>D5</td>
<td>2.17</td>
<td>37.96</td>
<td>5.25</td>
</tr>
<tr>
<td>D6</td>
<td>1.95</td>
<td>36.61</td>
<td>4.25</td>
</tr>
<tr>
<td>E1</td>
<td>0.97</td>
<td>35.91</td>
<td>5.81</td>
</tr>
<tr>
<td>E2</td>
<td>0.85</td>
<td>34.55</td>
<td>4.55</td>
</tr>
<tr>
<td>E3</td>
<td>0.75</td>
<td>33.43</td>
<td>3.55</td>
</tr>
<tr>
<td>E1*</td>
<td>1.02</td>
<td>37.67</td>
<td>6.17</td>
</tr>
<tr>
<td>E2*</td>
<td>0.97</td>
<td>36.04</td>
<td>4.75</td>
</tr>
<tr>
<td>E3*</td>
<td>0.87</td>
<td>35.22</td>
<td>3.96</td>
</tr>
<tr>
<td>F1</td>
<td>1.22</td>
<td>35.61</td>
<td>7.05</td>
</tr>
<tr>
<td>F2</td>
<td>1.07</td>
<td>35.30</td>
<td>6.55</td>
</tr>
<tr>
<td>F3</td>
<td>0.97</td>
<td>34.78</td>
<td>5.92</td>
</tr>
<tr>
<td>F1*</td>
<td>1.17</td>
<td>37.74</td>
<td>5.94</td>
</tr>
<tr>
<td>F2*</td>
<td>1.07</td>
<td>37.17</td>
<td>5.22</td>
</tr>
<tr>
<td>G1</td>
<td>0.62</td>
<td>36.10</td>
<td>7.39</td>
</tr>
<tr>
<td>G2</td>
<td>0.53</td>
<td>35.45</td>
<td>6.35</td>
</tr>
<tr>
<td>G3</td>
<td>0.45</td>
<td>35.35</td>
<td>5.86</td>
</tr>
</tbody>
</table>

Figure 5.27: Figure showing that the use of a constant value for the counterion adsorptivity for a series of coagulation experiments (using latex dispersion A) at different NaCl concentrations leads to deviations.
Since the optimal $K$-value is a function of both ionic strength and surface coverage at the beginning of the coagulation experiment, it is obvious that the counterion adsorption isotherm has a much more complex shape than the proposed Langmuirian one (Eqn. 3.22). Including the term $\exp\left(\frac{z_e e p}{k_B T}\right)$ to take into account electrostatic effects is not sufficient. Before proposing an alternative counterion adsorption isotherm, let us investigate the behaviour of the parameter $K$ in an alternative, direct way.

### 5.6.1 Zeta potential measurements at various NaCl concentrations

This section describes an alternative way to investigate the behaviour of $K$. Two different latex dispersions (B and F) were considered and the zeta potential of the polymer particles was measured at various NaCl concentrations. The characteristics of these two latex dispersions are taken from Table 5.2 and repeated in Table 5.10.

<table>
<thead>
<tr>
<th>index</th>
<th>average particle diameter, nm</th>
<th>solid weight fraction, 100 wt</th>
<th>g SDS used</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>75</td>
<td>16.31</td>
<td>7.5</td>
</tr>
<tr>
<td>F</td>
<td>114</td>
<td>14.82</td>
<td>1.5</td>
</tr>
</tbody>
</table>

**Table 5.10:** Characteristics of the two latex dispersions used for the zeta potential measurements at various NaCl concentrations.

The experimental procedure was the following:

1. 10 ml of concentrated NaCl solution was added to 50 ml of the original latex dispersion so that the resulting mixture (after a short time of stirring to achieve homogeneity) reaches the desired NaCl concentration (see Eqn. 5.1).

2. The resulting mixture was introduced in the ultrafiltration device and a sample of filtrate was collected. Since the addition of NaCl induces coagulation of the latex dispersion, low NaCl concentrations were chosen, and the ultrafiltration was performed during a short time.

3. A few drops of the original latex dispersion were added to the filtrate and the zeta potential was measured. The volume added is so small that the change of the NaCl concentration is negligible.

All experiments were performed at low NaCl concentrations to avoid coagulation. The results of the zeta potential measurements as a function of the NaCl concentration are reported in Table 5.11. Additionally, the corresponding ionic strengths $I$ and the bulk concentrations of the counterions $C_{Na^+}$ are given. The contributions to $I$ and $C_{Na^+}$ are
from the added NaCl, the residual initiator, and the emulsifier present in the aqueous phase.

<table>
<thead>
<tr>
<th>index</th>
<th>zeta potential, $\zeta$ (mV)</th>
<th>ionic strength, $I$ (mM)</th>
<th>$C_{Na^+}$ (mM)</th>
<th>counterion adsorptivity, $K \cdot 10^3$ (mM$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>55.93</td>
<td>11.45</td>
<td>7.82</td>
<td>147.3</td>
</tr>
<tr>
<td>B</td>
<td>49.69</td>
<td>39.87</td>
<td>36.24</td>
<td>22.5</td>
</tr>
<tr>
<td>B</td>
<td>40.53</td>
<td>68.39</td>
<td>64.76</td>
<td>16.7</td>
</tr>
<tr>
<td>B</td>
<td>36.23</td>
<td>96.94</td>
<td>93.31</td>
<td>12.7</td>
</tr>
<tr>
<td>B</td>
<td>33.77</td>
<td>125.47</td>
<td>121.86</td>
<td>9.9</td>
</tr>
<tr>
<td>B</td>
<td>30.65</td>
<td>154.04</td>
<td>150.41</td>
<td>9.0</td>
</tr>
<tr>
<td>F</td>
<td>40.76</td>
<td>11.026</td>
<td>7.392</td>
<td>124.6</td>
</tr>
<tr>
<td>F</td>
<td>32.74</td>
<td>39.33</td>
<td>15.7</td>
<td>20.7</td>
</tr>
<tr>
<td>F</td>
<td>29.26</td>
<td>67.66</td>
<td>64.02</td>
<td>10.6</td>
</tr>
<tr>
<td>F</td>
<td>19.85</td>
<td>95.90</td>
<td>92.15</td>
<td>14.5</td>
</tr>
<tr>
<td>F</td>
<td>18.52</td>
<td>124.32</td>
<td>120.68</td>
<td>10.8</td>
</tr>
<tr>
<td>F</td>
<td>14.00</td>
<td>152.65</td>
<td>149.01</td>
<td>13.4</td>
</tr>
</tbody>
</table>

Table 5.11: Results of the zeta potential measurements at various NaCl concentrations for the latex dispersions B and F.

Fig. 5.28 shows the measured zeta potential as a function of the ionic strength $I$. With the help of the set of equations given in section 3.3.2 we can evaluate the corresponding value of the Langmuir constant for counterion adsorption in Eqn. 3.22. The values of all model parameters used are given in Table 5.12. The values obtained for $K$ are also reported in Table 5.11 and plotted versus the ionic strength in Fig. 5.29. Similar to Fig. 5.26, the actual values of the emulsifier surface coverage ($\theta$) have been explicitly reported. Note that a larger $\theta$-variation is found here due to the relatively low salt concentrations used. At these salt concentrations, the maximum surface concentration $\gamma_\infty$ is still affected by the salt concentration and this explains the variation of $\theta$.

![Figure 5.28: Measured zeta potential of the latex dispersions B and F as a function of the ionic strength.](image-url)
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>relative permittivity of water</td>
<td>$\varepsilon=78$</td>
</tr>
<tr>
<td>polymer density</td>
<td>$\rho_p=1.05\text{ g.m}^{-1}$</td>
</tr>
<tr>
<td>(absolute) temperature</td>
<td>$T=298.15\text{ K}$</td>
</tr>
<tr>
<td>Stern layer thickness</td>
<td>$\delta=0.14\text{ nm}$</td>
</tr>
<tr>
<td>relative permittivity of Stern layer</td>
<td>$\varepsilon=78$</td>
</tr>
</tbody>
</table>

Table 5.12: Values of all model parameters used.

The initial zeta potentials for the latex dispersions that were presented in section 5.2.2 (Table 5.3) were calculated using the arithmetic mean (that is, 0.136 $mM^{-1}$) of the counterion adsorptivities derived from the zeta potential measurements without salt addition for the latex dispersions B and F. The calculated initial zeta potentials for these latex dispersions agree well with the zeta potentials measured; 55.93 $mV$ and 40.76 $mV$, respectively (see Fig. 5.28).

![Figure 5.29: Counterion adsorption isotherms derived from the zeta potential measurements at various NaCl concentrations versus the respective ionic strengths. The corresponding emulsifier surface coverages ($\theta$) are given in the legend.](image)

By inspection of the data in Fig. 5.29 it is readily understood that the counterion adsorption isotherm has a more complicated form than the proposed one, since the proposed Langmuir adsorption isotherm implies a constant value of $K$. The same conclusion was drawn from the $K$-values derived from the coagulation experiments. Fig. 5.30 shows both data sets and indicates an apparently discontinuous behaviour. However, plotting $K \cdot \exp\left( \frac{q_{\text{COH}}}{k_BT} \right)$ instead of $K$ shows a much more consistent relationship between the two data sets (see Fig. 5.31).
Figure 5.30: Counterion adsorptivities derived from both the coagulation experiments and the zeta potential measurements as a function of the ionic strength. The word "zeta" in the legend indicates that the values were calculated from the zeta potential measurements.

Figure 5.31: Plot of $K \cdot \exp\left(\frac{-\zeta_0 V}{k_B T}\right)$ for both the coagulation experiments and the zeta potential measurements as a function of the ionic strength. The word "zeta" in the legend indicates that the values were calculated from the zeta potential measurements.
5.6.2 An empirical model for the counterion adsorptivity

In this section an empirical relationship between the counterion adsorption constant, $K$, and the operating conditions (ionic strength $I$ and emulsifier surface coverage $\theta$) is proposed, since information in the literature does not provide us with reliable, predictive expressions and all experiments indicate that the counterion adsorptivity is clearly affected by parameters such as $I$ and $\theta$. As shown in Table 5.4 the surface coverage at the beginning of the coagulation experiments does not vary significantly for a series of coagulation experiments at different NaCl concentrations. Moreover, there is only a small sensitivity of the zeta potential to particle size, especially for large values of the dimensionless electrical double layer thickness, $\kappa a$. This is illustrated in Fig. 5.32 where the zeta potential versus particle size is shown for the initial conditions of coagulation experiment A1. For small particle sizes the zeta potential remains dependent on the particle size because $\kappa a$ has a smaller value.

![Zeta potential versus particle diameter at the beginning of coagulation experiment A1.](image)

Figure 5.32: Zeta potential versus particle diameter at the beginning of coagulation experiment A1.

For these reasons, $K$ versus the ionic strength for each series was fitted by an exponential curve in the form $a \cdot \exp(bI)$. It appears that the ratio $\kappa$ of the coefficients is a linear function of the surface coverage $\theta$, as can be seen in Fig. 5.33.
Figure 5.33: Ratio $\frac{a}{b}$ of the coefficients of the proposed expression for the counterion adsorption as a function of the emulsifier surface coverage.

The expression for $\frac{a}{b}$ as a function of $\theta$ is:

$$\frac{a}{b} = -2.945 \cdot \theta - 0.053$$  \hspace{1cm} (5.41)

Taking the value of $b$ constant and equal to the average of the fitted values (indicated as $\bar{b}$), provides us with an expression to estimate the Langmuir constant $K$ as a function of both $I$ and $\theta$ which best describes the $K$-values derived from the coagulation experiments. Hence, for $K$ we find:

$$K = \bar{b}(-2.945 \cdot \theta - 0.053) \exp(\bar{b}I)$$  \hspace{1cm} (5.42)

where $\bar{b} = -5.58 \cdot 10^{-3}$ $mM^{-1}$. In Figs. 5.34 to 5.36 the predicted values for $K$ are compared to those derived from the coagulation experiments. It is seen that the agreement is quite reasonable even though it has to be noted that even small differences in the value of $K$ already give rise to significant deviations in the prediction of the time evolution of the average particle size. See also Table 5.13 in the next section for the sensitivity of the stability ratio $W$ to the value of the counterion adsorption.
Figure 5.34: Comparison between the optimal $K$-values derived from the coagulation experiments (symbols) and the proposed empirical model (—). The results shown are for the latex dispersions A, D, E*, F, and F* with emulsifier surface coverages $\theta$ given in the legend.

Figure 5.35: Comparison between the optimal $K$-values derived from the coagulation experiments (symbols) and the proposed empirical model (—). The results shown are for the latex dispersions B and E with emulsifier surface coverages $\theta$ given in the legend.
Figure 5.36: Comparison between the optimal $K$-values derived from the coagulation experiments (symbols) and the proposed empirical model (—). The results shown are for the latex dispersions C and G with emulsifier surface coverages $\theta$ given in the legend.

Inserting the expression found for $K$ in Eqn. 3.22 enables us to formulate a modified counterion adsorption isotherm:

$$
\frac{\sigma_i}{\sigma_0} = \frac{b(-2.945 - \theta - 0.053) \exp(bI) c_{i,\infty} \exp \left( \frac{z_i e \phi_i}{k_B T} \right)}{1 + b(-2.945 - \theta - 0.053) \exp(bI) c_{i,\infty} \exp \left( \frac{z_i e \phi_i}{k_B T} \right)}
$$

(5.43)

It is seen that the exponential shape taking into account electrostatic effects is conserved and that the counterion adsorption equilibrium has become a function of the ionic strength $I$ and the emulsifier surface coverage $\theta$ at the beginning of the coagulation experiment. Since we used only the counterion adsorptivity values derived from the coagulation experiments to obtain the empirical model, a rather poor agreement with the values obtained directly from the measured zeta potential is expected. We verified that this is indeed the case.
5.7 Sensitivity study for the stability ratio $W$

This section presents the results of a sensitivity study especially regarding the stability ratio $W$ (Eqn. 3.59), but also for the counterion adsorptivity $K$ and the zeta potential $\zeta$. While the counterion adsorptivity was predicted according to the empirical model discussed in the previous section (Eqn. 5.42), the zeta potential was calculated using the Stern layer model presented in section 3.3.2. Coagulation experiment A3 is used as base case. The following experimental variables were varied: initial average particle diameter $d_0$, (absolute) temperature $T$, weight fraction of solids (wt) in the latex dispersion, amount of SDS used in the polymerization recipe ($g_{SDS}$), and concentration of the NaCl solution added to the latex dispersion (NaCl conc.). The sensitivities given in Table 5.13 are expressed as percentual differences from the values of the base case.

<table>
<thead>
<tr>
<th>variable</th>
<th>% change of counterion adsorptivity</th>
<th>% change of zeta potential</th>
<th>% change of $\log W$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_0$ - 5%</td>
<td>-4.67</td>
<td>-0.55</td>
<td>-7.30</td>
</tr>
<tr>
<td>$d_0$ - 2%</td>
<td>-1.86</td>
<td>-0.21</td>
<td>-2.92</td>
</tr>
<tr>
<td>$d_0$ + 2%</td>
<td>+1.86</td>
<td>+0.20</td>
<td>+2.93</td>
</tr>
<tr>
<td>$d_0$ + 5%</td>
<td>+4.64</td>
<td>+0.49</td>
<td>+7.33</td>
</tr>
<tr>
<td>$T$ - 5%</td>
<td>0</td>
<td>-4.31</td>
<td>-14.6</td>
</tr>
<tr>
<td>$T$ - 2%</td>
<td>0</td>
<td>-1.72</td>
<td>-5.78</td>
</tr>
<tr>
<td>$T$ + 2%</td>
<td>0</td>
<td>+1.71</td>
<td>+5.74</td>
</tr>
<tr>
<td>$T$ + 5%</td>
<td>0</td>
<td>+4.26</td>
<td>+14.25</td>
</tr>
<tr>
<td>wt - 5%</td>
<td>+7.47</td>
<td>+0.67</td>
<td>+3.18</td>
</tr>
<tr>
<td>wt - 2%</td>
<td>+2.89</td>
<td>+0.28</td>
<td>+1.28</td>
</tr>
<tr>
<td>wt + 2%</td>
<td>-2.78</td>
<td>-0.28</td>
<td>-1.28</td>
</tr>
<tr>
<td>wt + 5%</td>
<td>-6.74</td>
<td>-0.70</td>
<td>-3.20</td>
</tr>
<tr>
<td>$g_{SDS}$ - 5%</td>
<td>-5.04</td>
<td>-0.54</td>
<td>-2.20</td>
</tr>
<tr>
<td>$g_{SDS}$ - 2%</td>
<td>-2.02</td>
<td>-0.21</td>
<td>-0.85</td>
</tr>
<tr>
<td>$g_{SDS}$ + 2%</td>
<td>+2.02</td>
<td>+0.20</td>
<td>+0.83</td>
</tr>
<tr>
<td>$g_{SDS}$ + 5%</td>
<td>+5.05</td>
<td>+0.49</td>
<td>+2.02</td>
</tr>
<tr>
<td>NaCl conc. - 5%</td>
<td>+7.33</td>
<td>+0.59</td>
<td>+4.84</td>
</tr>
<tr>
<td>NaCl conc. - 2%</td>
<td>+2.87</td>
<td>+0.22</td>
<td>+1.86</td>
</tr>
<tr>
<td>NaCl conc. + 2%</td>
<td>-2.79</td>
<td>-0.20</td>
<td>-1.74</td>
</tr>
<tr>
<td>NaCl conc. + 5%</td>
<td>-6.83</td>
<td>-0.46</td>
<td>-4.19</td>
</tr>
</tbody>
</table>

Table 5.13: Results of a sensitivity study regarding counterion adsorptivity, zeta potential, and stability ratio using coagulation experiment A3 as base case.

By inspection of the $W$-values in the table the strong sensitivity to temperature is apparent, i.e. the system is destabilized by cooling. Since a decrease of temperature results in a corresponding reduction of the particle diffusion coefficients, this effect is mainly related to the effect of temperature on the potential energy of interaction. The
sensitivity to emulsifier amount and salt concentration are as expected. The significant size effect can be simply explained as the usual increase of the stability ratio when increasing the particle size (see Figs. 3.14 and 3.15).

Concerning the countercation adsorptivity, \( K \), the sensitivity to temperature is zero simply because the thermal effect was not included in the empirical model. Maximum sensitivity is verified with respect to the variations of salt concentration and weight fractions of solid. These effects are practically equivalent and this is explained in terms of the resulting salt concentration in the aqueous phase (indirectly affected by the weight fraction solids which modifies the water hold-up).

A large sensitivity to temperature is observed also in the case of the zeta potential. On the other hand, \( \zeta \) is not very sensitive to variations of the remaining quantities and, in particular, it is only weakly affected by the particle size. The last aspect could be expected since the value of the dimensionless electrical double layer thickness \((\kappa a)\) in Eqn. 3.30 is much larger than 1.

Finally, it is worth mentioning that the aim of this analysis was to better identify the key parameters to be kept under control during the coagulation experiments. The conclusive indication here is that accurate temperature control can be important and that future experiments have to consider better this aspect.
Seite Leer / Blank leaf
Chapter 6

Conclusions

In this work a comprehensive model for particle coagulation in polymeric lattices subject to turbulent flow has been developed. It is based on the description by a convection-diffusion equation for a single pair of particles embedded in an extensional flow field which we assume to represent well the microflow on the scale below the Kolmogorov scale. The required input parameter, the local average rate of energy dissipation, $\epsilon$, can be estimated via common methods known in chemical engineering (LDV, CFD). Also for the other two particle transport mechanisms, Brownian diffusion and particle motion induced by colloidal particle interaction, the hydrodynamic interaction between the two particles is properly taken into account. Simulations using the convection-diffusion equation show that the rate of coagulation is sensitive to fluid motion mainly for colloidal systems where the electrical double layer is thick. Although larger particle sizes are more stable from a colloidal point of view, the rate of aggregation may increase with particle size when the electrical double layer is relatively thick and the flow field is sufficiently intense. This provides information on the way emulsion polymerization reactors should be operated to guarantee stability with respect to particle coagulation. Because of the demanding numerical effort to solve the convection-diffusion equation, two simplified coagulation models were developed that involve only ordinary differential equations but still take into account all particle transport mechanisms. For the first simplified model, where the extensional flow field is split into two regions and averaged differential equations are solved, a very good agreement is found with the predictions obtained from the detailed model. Alternatively, the second simplified model where gradient diffusion is used as closure for the turbulent particle transport term, is shown to work properly only for colloidal unstable systems. The evolution in time of the particle size distribution is predicted with the help of a population balance equation and it was shown that a particular form of this equation is required
to take into account effects of all features of turbulent flow on particle coagulation. The population balance can be employed mainly for the initial stage where doublet formation dominates due to the underlying particle coagulation model that was developed here. To validate the model predictions, perikinetic coagulation experiments induced by NaCl addition were carried out with well-characterized initial polystyrene latex dispersions stabilized with an ionic emulsifier (SDS). Different values of emulsifier surface coverage and particle size were examined at different NaCl concentrations. An empirical model for the adsorption of counterions in the Stern layer was formulated and the model parameters were identified by comparison between the experimentally measured evolution of the average particle size and the predicted one. With this model the zeta potential, a key parameter with respect to latex stability, can be predicted. The predicted time evolution of the whole particle size distribution provided better understanding of the observed coagulation behaviour, such as the formation of a multimodal particle size distribution.

In future work we will try to obtain from the simplified models explicit analytical expressions, not involving differential equations, for the rate of coagulation. Additionally, novel kinds of simplified models using alternative closure expressions for the turbulent particle transport term will be investigated. The coagulation model is intended to include a better picture of particle morphology so as to describe properly the coagulation of particles other than singlets. Coagulation experiments will be carried out where fluid motion plays a role to validate the predictions of the complete model for the rate of coagulation. Due to the occurrence of turbulent intermittency, as well as the inhomogeneous distribution of local average values of $\epsilon$, the complete spectrum of the energy dissipation will be taken into account instead of using a single average value. To achieve a better understanding of the Stern layer submodel, in particular concerning the counterion adsorption isotherm, the time evolution of the average particle size and the zeta potential during a coagulation experiment will be followed simultaneously. It is foreseen that these future activities will lead to an even more comprehensive model for particle coagulation in dispersed systems.
Appendix A

Hydrodynamic interaction functions for diffusion

A lengthy, but exact series solution for the hydrodynamic interaction function $G(r, \lambda)$ was given by Spielman (1970) (for the sake of brevity this solution will not be reproduced here). Honig et al. (1971) approximated this series solution by a single, much more convenient expression differing about 1% only for equal-sized particles:

$$G(h_2, \lambda) = \frac{h_2^2 + \frac{2}{3}h_2}{h_2^2 + \frac{13}{3}h_2 + \frac{1}{3}}$$  \hspace{1cm} (A.1)

in which $h_2$ is the dimensionless surface-to-surface distance: $h_2 = \frac{2r}{a_1+a_2} - 2$. Comparing this to the Spielman solution and to the numerical results by Batchelor (1976) shows that for equal-sized particles this is the case indeed (see Fig. A.1).

**Figure A.1:** The hydrodynamic interaction function $G$ for equal-sized particles as a function of the dimensionless surface-to-surface distance $h_2$ (Batchelor numerical solution (xx), Spielman series solution (oo), fit expression used here (—)).
For equal-sized particles the hydrodynamic interaction function $G(r, \lambda = 1)$ is also available as a series expression:

$$G(x, \lambda = 1) = \frac{1}{g_2(x)}$$  \hspace{1cm} (A.2)

in which $x = \frac{r}{a_1}$ and the function $g_2(x)$ is given as a series expression by Eqn. B.5 in appendix B (taken from van de Ven (1989) and Elimelech et al. (1995)). The agreement of Eqn. A.1 with the Spielman solution is poor for unequal-sized particles. To obtain a better expression for $G(r, \lambda)$ the following strategy was adopted. We replaced the constant parameters $\frac{2}{3}, \frac{13}{6}, \text{and} \frac{1}{3}$ in Eq. A.1 by the functions $a$, $b$, and $c$ that depend on the size ratio $\lambda$. Fitting this expression to data obtained from the Spielman solution for different size ratios yields a set of parameters that can be correlated with themselves and with $\lambda$. In quite good approximation for all size ratios we get:

$$a(\lambda) = \frac{\exp(1)}{2} \lambda_1 \frac{\lambda_1 + 2}{\lambda_1 + 2}$$  \hspace{1cm} (A.3)

$$b(\lambda) = \exp(1) - a(\lambda)$$  \hspace{1cm} (A.4)

$$c(\lambda) = a(\lambda) \left(\frac{\lambda_1}{2} + 1\right)^{-1}$$  \hspace{1cm} (A.5)

where $\lambda_1 = \lambda + \lambda^{-1}$ indicating symmetry with respect to $\lambda$. Note that for $\lambda = 1$ the functions $a(\lambda)$, $b(\lambda)$, and $c(\lambda)$ approach quite nicely the parameters of the Honig expression (Eqn. A.1). Note that when the size ratio $\lambda$ is exactly equal to 0 the hydrodynamic interaction function becomes equal to 1 for all distances. This can simply be understood since when $\lambda = 0$ the binary system reduces to a single particle system. Fig. A.2 shows $G(r, \lambda)$ as a function of the dimensionless surface-to-surface distance $h$ for various size ratios as well as the Spielman solution and the numerical results of Batchelor. It is seen that using a value of 1 for the hydrodynamic interaction function is without doubt incorrect and that it is essential to take into account the dependence on both distance and size ratio.
Concerning the reduction of tangential diffusion $D_\theta$ by hydrodynamic interaction Batchelor (1976) gives numerical results for equal-sized particles. Since tangential diffusion was not included in the governing equations for relative particle motion a general expression for different size ratios was not sought for. However, to support the order of magnitude analysis performed in section 3.6, $H$ as a function of $h$ was already shown in Fig. 3.7 for equal-sized particles.
Seite Leer /
Blank leaf
Appendix B

Hydrodynamic interaction functions for convective motion

For the mobility function $A(r, \lambda)$ (radial direction) several theoretical expressions are available from Batchelor and Green (1972). Unfortunately, none of them spans the complete range of $r$ and $\lambda$-values:

(i) For the far field ($r \gg a_1 + a_2$):

$$A(x, \lambda) = \frac{\lambda}{2} \left(1 + \lambda^2 \right) - \frac{3}{2} \left(1 + \lambda^5 \right) + \frac{5}{2} \lambda^2 \left(1 + \lambda \right)$$

in which $x = \frac{r}{a_1}$ is the dimensionless center-to-center distance. Additional higher order terms in this expression can be found in Kim and Karrila (1991). Although Eqn. B.1 is suitable for the far field Batchelor and Green note that this expression still works reasonably well when the particles are in close proximity.

(ii) For the limiting case $\lambda \to 0$ (complete field):

$$A(x, \lambda \to 0) = \frac{5}{2x^3} - \frac{3}{2x^5}$$

in which $x = \frac{r}{a_1}$. In this case the smallest particle does not disturb the flow.

(iii) For equal-sized particles (complete field) (taken from van de Ven and Mason, 1976):

$$A(x, \lambda = 1) = 1 - \frac{2 g_1(x)}{\pi g_2(x)}$$

where:

$$g_1(x) = \frac{4}{3} \sinh^4 \xi \sum_{n=1}^{\infty} \frac{n(n+1)(2n+1)}{\Delta_n}$$

and:

$$g_2(x) = \frac{4}{3} \sinh \xi \sum_{n=1}^{\infty} \frac{n(n+1)}{2\Delta_n} \left[ \frac{2n+1}{2(2n-1)} \exp(2\xi) + \frac{2n+1}{2(2n+3)} \exp(-2\xi) \\
+ \frac{4\exp(-(2n+1)\xi)}{(2n-1)(2n+3)} - 1 \right]$$
in which:

$$\Delta_n = 2 \sinh((2n + 1)\xi) - (2n + 1) \sinh(2\xi)$$  \hspace{2cm} (B.6)

and,

$$\xi = \cosh^{-1}\left(\frac{x}{2}\right)$$  \hspace{2cm} (B.7)

(iv) For the near field ($h \to 0$) and $\lambda = 1$:

$$A(h, \lambda = 1) = 1 - 4.077h + O(h^{3/2})$$  \hspace{2cm} (B.8)

in which $h = \frac{2r}{a_1 + a_2} - 2$ is the dimensionless surface-to-surface distance, here equal to $x - 2$. Kim and Karrila (1991) give additional, empirical expressions for other $\lambda$-values using $h \cdot \ln(h^{-1})$ for the $O(h^{3/2})$ term.

Some numerical data obtained by solving directly the equations of motion for a pair of force- and torque-free particles have been published by Lin et al. (1970) and Batchelor and Green (1972) for $\lambda = 1$, and by Adler (1981a) for $\lambda = 0.5, 0.2, 0.1$ and 0.05.

As a consequence of this lack of information the following approach is proposed.

The question arises which kind of objective function for $A(r, \lambda)$ to use. First, we notice that the first two terms of the far field expression (i, Eqn. B.1) have the same shape as the complete field expression for $\lambda = 0$ (ii, Eqn. B.2). In analogy with the way $G(r, \lambda)$ was obtained in appendix A an objective function is used replacing $\frac{8}{2}$ and $-\frac{3}{2}$ by functions $d$ and $e$ that are a function of the size ratio $\lambda$. Second, we can make use of the constraint that -for all size ratios- $A$ is zero when the two particles touch, i.e. for $x = 1 + \lambda$. Moreover, for $\lambda = 0$ the parameters $d$ and $e$ should equal $\frac{8}{2}$ and $-\frac{3}{2}$, respectively.

Values for $A(r, \lambda)$ in the complete field for several size ratios were obtained using numerical solution of the equations of motion implemented by Kim (see Kim and Karrila, 1991). The resulting fit functions $d(\lambda)$ and $e(\lambda)$ are:

$$d(\lambda) = -1.5288\lambda^0 + 5.3015\lambda^3 - 7.5523\lambda^4 + 8.8665\lambda^5$$  \hspace{2cm} (B.9)

$$- 5.0633\lambda^2 - 0.332\lambda + 2.5058$$

$$e(\lambda) = (1 + \lambda)^5 - d(\lambda)(1 + \lambda)^2$$  \hspace{2cm} (B.10)

In Figs. B.1 to B.5 the general expression obtained for $A(r, \lambda)$ is compared to the numerical results and the available literature data. It is seen that the agreement is quite good.

Additionally, for equal-sized particles the obtained general expression for $A(r, \lambda)$ is close to the series solution (iii, Eqn. B.3). Moreover, the mobility function for $\lambda = 0.05$ is almost the same as for the case $\lambda \to 0$ as can be seen from Fig. B.5.
Figure B.1: The mobility function $A$ for equal-sized particles; Batchelor and Green ($\infty$), using Kim's code (—), fit expression used here (---).

Figure B.2: The mobility function $A$ for particles with size ratio $\lambda = 0.5$; Adler (□□), using Kim's code (—), fit expression used here (---).
Figure B.3: The mobility function $A$ for particles with size ratio $\lambda = 0.2$; Adler (□□), using Kim's code (—), fit expression used here (---).

Figure B.4: The mobility function $A$ for particles with size ratio $\lambda = 0.1$; Adler (□□), using Kim's code (—), fit expression used here (---).
As mentioned, for the mobility function $B(r, \lambda)$ (tangential direction) the situation is similar.

(i) For the far field the following expression holds (see Kim and Karrilla (1991), also to include higher order additional terms):

$$B(x, \lambda) = \frac{3(1 + \lambda)^5 + 5\lambda^2(1 + \lambda)}{3x^5} + \frac{5\lambda^3(1 + \lambda^2)}{3x^8} \quad (B.11)$$

(ii) For the complete field in the limit $\lambda \to 0$:

$$B(x, \lambda \to 0) = \frac{1}{x^5} \quad (B.12)$$

where $x = \frac{r}{a_1}$.

(iii) For equal-sized particles (complete field):

$$B(x, \lambda = 1) = 1 - \frac{r_e(x)^2 - 1}{r_e(x)^2 + 1} \quad (B.13)$$

in which $x = \frac{r}{a_1}$ and $r_e(x)$ is the equivalent spheroidal axis ratio of the two spheres (Bartok and Mason, 1957). For $r_e(x)$ no complete analytical expression is available, but asymptotic expressions for large (see i, Eqn. B.11) and small separations are available. Tabulated values are given by Batchelor and Green (1972).
Along with the numerical results for $A(r, \lambda)$ the simulation with Kim's code yields values for $B(r, \lambda)$. Unfortunately, contrary to the mobility function for the radial direction, $B(r, \lambda)$ in general does not approach 1 when the two particles touch. Reason for this is that the particles can "roll" over one another. An exception is when one of the particles is much smaller than the other one.

For the objective function we replace the 1 in Eqn. B.12 by a function $f(\lambda)$ and add to this the term $\frac{g(\lambda)}{x^2}$ (this term is absent for $\lambda \to 0$).

The resulting fit expressions for $f(\lambda)$ and $g(\lambda)$ are:

$$f(\lambda) = -64.116\lambda^6 + 196.62\lambda^5 - 230.72\lambda^4 + 127.8\lambda^3 - 29.744\lambda^2 + 0.1104\lambda + 1$$

$$g(\lambda) = (1 + \lambda)^{\beta} B_{\text{touch}}(\lambda) - f(\lambda)(1 + \lambda)^3$$

in which $B_{\text{touch}}(\lambda)$ is the fit expression for $B$ upon touching:

$$B_{\text{touch}}(\lambda) = 12.256\lambda^6 - 41.476\lambda^5 + 55.028\lambda^4 - 36.715\lambda^3 + 13.905\lambda^2 - 3.7156\lambda + 1$$

A comparison between the fit expression for $B(r, \lambda)$ and the numerical results obtained with Kim's code is given in Figs. B.6 to B.10. Added to this were the numerical results obtained by Lin et al. (1970) and Batchelor and Green (1972) for $\lambda = 1$ and by Adler (1981a) for $\lambda = 0.5, 0.2, 0.1$ and 0.05. Again, acceptable agreement is achieved for all size ratios. Similar to the mobility function $A$ for $\lambda = 0.05$, $B$ does not differ much from the mobility function when one of the two particles is much smaller than the other one, i.e. $\lambda \to 0$ (see Fig. B.10).
Figure B.6: The mobility function $B$ for equal-sized particles; Batchelor and Green, Lin ($\infty$), using Kim's code ($\cdot$), fit expression used here (---).

Figure B.7: The mobility function $B$ for particles with size ratio $\lambda = 0.5$; Adler (□□), using Kim's code ($\cdot$), fit expression used here (---).
Figure B.8: The mobility function $B$ for particles with size ratio $\lambda = 0.2$; Adler (□□), using Kim's code (—), fit expression used here (---).

Figure B.9: The mobility function $B$ for particles with size ratio $\lambda = 0.1$; Adler (□□), using Kim's code (—), fit expression used here (---).
Figure B.10: The mobility function $B$ for particles with size ratio $\lambda = 0.05$: Adler (□□), using Kim's code (---), fit expression used here (----). The points indicated with an asterix refer to the case $\lambda \to 0$. 
Appendix C

Behaviour of the ratio \( \frac{1-A}{G} \)

In appendices A and B general expressions for the hydrodynamic interaction function \( G(r, \lambda) \) (for Brownian diffusion in the radial direction) and for the mobility function \( A(r, \lambda) \) (for convective motion in the radial direction) were derived. Note that when the two particles touch the nominator as well as the denominator of the ratio \( \frac{1-A}{G} \) approach zero. In Fig. C.1 the calculated ratio \( \frac{1-A}{G} \) for various size ratios is shown as a function of the dimensionless distance of separation. Additionally, using numerical values for \( A \) presented by Adler (1981a) and Batchelor and Green (1972) and the exact series solution for \( G \) by Spielman (1970), the discrete values of \( \frac{1-A}{G} \) for the same size ratios are obtained. Note that for equal-sized particles these values are the same as those calculated by Zeichner and Schowalter (1977). Moreover, employing the series solutions for \( G(r, \lambda) \) and \( A(r, \lambda) \) given by Eqns. A.2 and B.3, respectively, yields the following expression for the ratio \( \frac{1-A}{G} \) for the complete region for equal-sized particles:

\[
\frac{1-A}{G} = \frac{2}{x} g_1(x)
\]  

(C.1)

This expression agrees with the ratio derived from literature data for equal-sized particles as can be seen from Fig. C.1. The ratio \( \frac{1-A}{G} \) varies between 0 and 2 for size ratios \( \lambda \) between 0 and 1, respectively. Care must be taken with the calculated ratio at short distances of separation. The reason is that the calculated ratio does not always approach the proper limiting value upon touching and is not always monotonic. Despite this behaviour of \( \frac{1-A}{G} \), the results obtained with the turbulent diffusion model (see section 4.1) indicate that the calculated rate of aggregation is not affected.
Figure C.1: The ratio $\frac{(1-A)}{G}$ as a function of the dimensionless surface-to-surface distance $h_2$; values derived from literature data (symbols) and the expression used in this study (---). The series solution for equal-sized particles is the dashed curve.
Bibliography


[37] Landgrebe, J.D. and S.E. Pratsinis, "A discrete sectional model for particulate production by gas phase chemical reaction and aerosol coagulation in the free molecular regime.", J. Colloid Interface Sci. 139, 63-86 (1990).


# Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>characteristic length, $a = \frac{a_1 + a_2}{2}$, or particle radius (m)</td>
</tr>
<tr>
<td>$a_i$</td>
<td>radius of particle $i$ (m)</td>
</tr>
<tr>
<td>$a(v, x_i)$</td>
<td>fraction of particles formed by coagulation assigned to class $i$ and born in size range $(x_i - x_{i+1})$</td>
</tr>
<tr>
<td>$a, b$</td>
<td>coefficients in the empirical model for the counterion adsorptivity $(mol/m^3w)^{-1}$</td>
</tr>
<tr>
<td>$a, b$</td>
<td>functions used for the presumed tangential concentration profile in region 1 $(kg/m^3w)$</td>
</tr>
<tr>
<td>$a, b, c$</td>
<td>functions used in the expression for the hydrodynamic interaction function $G$ (–)</td>
</tr>
<tr>
<td>$A(r, \lambda)$</td>
<td>mobility function for (relative) radial particle velocity (–)</td>
</tr>
<tr>
<td>$A_0$</td>
<td>molecular area of surfactant at saturation adsorption $(m^2)$</td>
</tr>
<tr>
<td>$A$</td>
<td>characteristic acceleration $(m/s^2)$</td>
</tr>
<tr>
<td>$b(v, x_i)$</td>
<td>fraction of particles formed by coagulation assigned to class $i$ and born in size range $(x_i - x_{i+1})$</td>
</tr>
<tr>
<td>$B(\tau, \lambda)$</td>
<td>mobility function for (relative) tangential particle velocity (–)</td>
</tr>
<tr>
<td>$B_{touch}$</td>
<td>value of the mobility function $B$ when the two particles touch (–)</td>
</tr>
<tr>
<td>$B$</td>
<td>constant of proportionality in the expression for the rate of dissipation (–)</td>
</tr>
<tr>
<td>$C_{e,w}$</td>
<td>emulsifier concentration in the aqueous phase $(mol/m^3w)$</td>
</tr>
<tr>
<td>$C_{e,tot}$</td>
<td>total emulsifier concentration in the latex dispersion $(mol/m^3w)$</td>
</tr>
<tr>
<td>$C_{\text{NaCl}}$</td>
<td>NaCl concentration in the aqueous phase $(mol/m^3w)$</td>
</tr>
<tr>
<td>$c_i$</td>
<td>concentration of particle $i$ $(kg/m^3w)$</td>
</tr>
<tr>
<td>$c_{i,\infty}$</td>
<td>bulk concentration of ions of type $i$ $(mol/m^3w)$</td>
</tr>
<tr>
<td>$d$</td>
<td>particle diameter (m)</td>
</tr>
<tr>
<td>$d$</td>
<td>function used for the presumed tangential concentration profile in region 2 $(kg/m^3w)$</td>
</tr>
<tr>
<td>$d, e$</td>
<td>functions used in the expression for the mobility function $A$ (–)</td>
</tr>
<tr>
<td>$D$</td>
<td>(mutual) diffusion coefficient $(m^2/s)$</td>
</tr>
<tr>
<td>$D_t$</td>
<td>turbulent diffusivity $(m^2/s)$</td>
</tr>
<tr>
<td>$e$</td>
<td>charge of electron, $e = 1.602 \cdot 10^{-19} , C$</td>
</tr>
<tr>
<td>$E, E_{33}$</td>
<td>rate of extension of vortex lines $(s^{-1})$</td>
</tr>
<tr>
<td>$E_{ij}$</td>
<td>element $(i, j)$ of the deformation (rate of strain) tensor $\mathbf{E} (s^{-1})$</td>
</tr>
<tr>
<td>$f$</td>
<td>dimensionless colloidal force of interaction</td>
</tr>
</tbody>
</table>
\( f(m,t), f(v,t) \) number density function at time \( t \) in terms of particle mass, \( m \), and volume, \( v \) (\#/kg, \#/m^3)

\( f(\xi,t) \) particle population distribution, average number of particles per unit volume of the particle state space

\( f, g \) functions used in the expression for the mobility function \( B (-) \)

\( F(r) \) particle radius distribution (\#/m)

\( g_j \) growth rate along the \( j \)-th characteristic axis of the particle

\( g_m \) rate of increase of particle mass (kg/s)

\( g_1(x) \) series expression used to calculate \( A \) for equal-sized particles

\( g_2(x) \) series expression used to calculate \( G \) and \( A \) for equal-sized particles

\( g(Q*, \tau) \) (normalized) temporal autocorrelation function of the scattering intensity (-)

\( g_{SDS} \) amount of SDS used in the polymerization recipe (g)

\( G(r, \lambda) \) hydrodynamic interaction function for radial particle diffusion (-)

\( G(\Gamma) \) weight function, relative scattering contribution (m^{-1})

\( \eta \) dimensionless gap between two particles, \( \eta = \frac{r-a_1-a_2}{a_1} = \frac{r}{a_1} - 1 - \lambda \)

\( \eta_1 \) surface-to-surface distance between two particles, \( \eta_1 = r - a_1 - a_2 \) (m)

\( \eta_2 \) dimensionless surface-to-surface distance, \( \eta_2 = \frac{2r}{a_1+a_2} - 2 \)

\( h(\xi,t) \) rate of change of the number of particles with phase coordinate \( \xi \) within the system at time \( t \)

\( H(r, \lambda) \) hydrodynamic interaction function for tangential particle diffusion (-)

\( H_a \) Hamaker constant (J)

\( I \) ionic strength, \( I = \frac{1}{2} \sum_i z_i^2 c_i \infty \) (mol/m^3w)

\( I(Q, \tau) \) scattering intensity (m^{-1})

\( \overline{\eta} \) unit second-order tensor

\( k_B \) Boltzmann constant, \( k_B = 1.38 \cdot 10^{-23} \) J/K

\( K \) counterion adsorptivity ((mol/m^3w)^{-1})

\( K_1, K_2 \) parameters for the SDS adsorption isotherm ((mol/m^3w)^{-1})

\( K_\ast \) Rayleigh scattering intensity of a single particle (m^{-4})

\( L \) characteristic size or length (m)

\( m \) particle mass (kg)

\( m \) ratio of polymer and medium refractive indices, \( m = \frac{\beta}{n_0} \)

\( M(t) \) amount of monomer in the system at time \( t \) (kg)

\( n \) polymer refractive index (-)
\( n_i \) number distribution for ions of type \( i \) (\#/m^3w)
\( n_0 \) refractive index of the medium (-)
\( n_p \) number of polymer particles per unit volume of continuous phase (\#/m^3w)
\( N \) number of classes for discretization of the distribution \( f(\upsilon, t) \)
\( N_{Av} \) Avogadro number, \( N_{Av} = 6.023 \cdot 10^{23} \) #/mol
\( N_i \) particle (population) flux in direction \( i \) (kg/m^2/s)
\( N_i \) number of particles in class \( i \), \( v_i \leq x_i \leq v_{i+1} \) where \( x_i \) is pivot volume \( i \)
\( N_2(t) \) total number of particles of type 2 in the system at time \( t \) (#)
\( p(\mathbf{r}^2, \lambda, t) \) conditional pair distribution function
\( P(Q_0, a) \) form factor (-)
\( Q_* \) scattering vector, \( Q_* = \frac{4\pi n_0}{\lambda_0} \sin \frac{\theta}{2} \) (m\(^{-1}\))
\( r \) center-to-center distance, particle radius (m)
\( r_e \) equivalent spheroidal axis ratio (-)
\( r_m \) rate of formation of nuclei with mass \( m \) (#/kg/s)
\( R \) radius of collision surface, \( R = a_1 + a_2 \) (m)
\( R_h \) hydrodynamic radius as measured by DLS (m)
\( \mathbf{s} \) property (internal) coordinates, \( \mathbf{s} = [s_1, s_2, \ldots] \)
\( S \) minus the "skewness factor" of the rate of extension in a fixed direction (-)
\( S_p \) specific particle surface (m^2/m^3w)
\( t \) time (s)
\( T \) (absolute) temperature (K)
\( u_i \) velocity of ion of type \( i \) (m/s)
\( u' \) turbulent rms velocity fluctuation (m/s)
\( \mathbf{u}(\mathbf{\zeta}, t) \) particle state velocity vector (m/s)
\( U \) characteristic velocity (m/s)
\( v \) particle volume, \( v = \frac{1}{3}\pi r^3 \) for spherical shape (m^3)
\( v_i \) particle velocity in physical space in direction \( i \) (m/s)
\( V_\xi \) electrophoretic mobility, \( V_\xi = \frac{\xi}{\mathcal{E}} \) (m^2/s/V)
\( Q \) rate of coagulation (kg/s)
\( wt \) weight fraction of solids in a latex dispersion, \( 0 < wt < 1 \) (-)
\( W \) stability ratio (-)
\( x \) dimensionless center-to-center distance between two particles, \( x = \frac{r_0}{a_1} \)
\( x \) volume fraction of continuous phase (\( m^3 w/m^3-disp \))

\( x_i \) pivot volume \( i (m^3) \)

\( \vec{x} \) spatial (external) coordinates, \( \vec{x} = [x_1, x_2, x_3] \)

\( X \) degree of monomer conversion, \( 0 \leq X \leq 1 (-) \)

\( X_A \) surface fraction inflow (upstream) region (-)

\( z \) variable in the gamma distribution, \( z = \lambda \nu / \bar{\sigma} (-) \)

\( z_j \) valence of ion \( j \)

**Greek symbols**

\( \alpha \) constant of proportionality in the expression for the turbulent diffusivity (-)

\( \beta(m, m') \) aggregation frequency of particles having mass \( m \) and \( m' \), respectively (s\(^{-1}\))

\( \delta \) outer Stern layer thickness (m)

\( \epsilon \) local average rate of dissipation of turbulent kinetic energy (W/kg)

\( \epsilon \) permittivity of the dielectric medium, \( \epsilon = \epsilon_r \epsilon_0 \) (SI-units) (C/V/m)

\( \epsilon_0 \) permittivity of vacuum, \( \epsilon_0 = 8.854 \cdot 10^{-12} \) C/V/m

\( \epsilon_r \) relative permittivity (-)

\( \epsilon_S \) permittivity of the outer Stern layer (C/V/m)

\( \xi \) external electrical field (V/m)

\( \phi^* \) volume fraction polymer in a monomer-swollen particle (-)

\( \Phi \) ratio between the surface potentials, \( \Phi = \frac{\Phi_{i2}}{\Phi_{i1}} \) (-)

\( \Phi_{i1} \) electric surface potential at surface \( i \) (V)

\( \gamma \) emulsifier surface concentration (mol/m\(^2\))

\( \gamma_i \) surface concentration of counterions of type \( i \) at the IHP (mol/m\(^2\))

\( \gamma_\infty \) maximum emulsifier surface concentration (mol/m\(^2\))

\( \gamma(m, m') \) number of fragments with mass \( m \) after breakup of a particle with mass \( m' \) (#)

\( \Gamma \) decay rate of the scattering contribution, \( \Gamma = \mathcal{D} Q_4^2 \) (s\(^{-1}\))

\( \Gamma(m) \) breakup frequency of a particle with mass \( m \) (s\(^{-1}\))

\( \kappa \) Debye-Hückel constant, \( \kappa = \frac{\sqrt{2e^2N A k_B T}}{e k_B T} \) (m\(^{-1}\))

\( \lambda \) size ratio, \( \lambda = \frac{a_2}{a_1} (-) \)

\( \lambda \) parameter of the gamma distribution, \( \lambda = \frac{1}{\bar{\nu} \bar{\sigma}} (-) \)

\( \lambda_0 \) vacuum wavelength of the light (m)
λ₁ parameter in the expression for \( G \), \( \lambda₁ = \lambda + \frac{1}{\lambda} \) (–)

\( \lambda_\theta \) Taylor microscale of turbulence (\( m \))

\( \lambda_i \) wavelength of the incident light (\( m \))

\( \lambda_K \) Kolmogorov microscale of turbulence, \( \lambda_K = \left( \frac{v^3}{\nu} \right)^{1/4} (m) \)

\( \lambda_n \) moment of order \( n \) of the particle radius distribution \( F(\tau) \) (\( \# \cdot m^n \))

\( \mu \) dynamic fluid viscosity (\( Pa \cdot s \))

\( \mu_\alpha(t) \) moment of order \( \alpha \) of the particle volume distribution \( f(v) \) at time \( t \) (\( \# \cdot m^{3\alpha} \))

\( \nu \) kinematic fluid viscosity, \( \nu = \frac{\mu}{\rho} (m^2/s) \)

\( \theta \) emulsifier surface coverage, \( \theta = \frac{\rho}{\rho_\infty} (-) \)

\( \theta \) angle of observation in the expression for the scattering vector \( Q \), (\( rad \))

\( \rho \) charge density (\( C/m^3 \))

\( \rho \) fluid density (\( kg/m^3 \))

\( \rho_i \) correction factor accounting for the tangential particle concentration profile in region \( i \) (–)

\( \rho_j \) density of material with index \( j \) (\( kg/m^3 \))

\( \sigma \) coefficient of variation or polydispersity index (–)

\( \sigma_i \) charge density at surface \( i \) (\( C/m^2 \))

\( \sigma^2 \) variance of the number density function \( f(m,t) \) (\( kg^2 \))

\( \tau \) time interval (\( s \))

\( \tau_{av} \) averaging time (\( s \))

\( \tau_B \) characteristic time for Brownian diffusion, \( \tau_B = \frac{v^2}{\nu} (s) \)

\( \tau_E \) characteristic time for elongation, \( \tau_E = \left( \frac{1}{\beta^{3/2}} \right) \sqrt{\frac{\rho}{\rho_\infty}} (s) \)

\( \tau_K \) Kolmogorov time microscale, \( \tau_K = \sqrt{\frac{\nu}{\epsilon}} (s) \)

\( \tau_L \) Lagrangian time microscale (\( s \))

\( \tau_{\theta} \) strain rate correlation time (\( s \))

\( \tau_{1/2} \) characteristic time for coagulation, \( \tau_{1/2} = \frac{1}{3N_{20}} (s) \)

\( \bar{\omega} \) angular velocity (or spin) vector (\( rad/s \))

\( \bar{\Omega} \) rotation tensor (\( rad/s \))

\( \xi \) dimensionless center-to-center distance, \( \xi = \frac{\xi}{\rho} \)

\( \xi \) variable in the expression for the mobility function \( A \) for equal-sized particles, \( \xi = \cosh^{-1}\left( \frac{3}{2} \right) (-) \)

\( \bar{\xi} \) particle state (or phase) space, \( \bar{\xi} = [\vec{x}, \vec{\xi}] \)
\( \psi \)  
potential energy of interaction (\( J \))

\( \zeta \)  
zeta potential (\( V \))

**Sub- and superscripts**

- **add** indicates added solution
- **attr** attraction
- **cont** continuous
- **cr** critical
- **d** refers to OHP
- **disp** dispersion
- **i** refers to IHP
- **int** interaction
- **L** refers to fluid
- **m** refers to monomer
- **p** refers to polymer
- **ppm** indicates that ppm units are used
- **rep** repulsion
- **T** transpose of a tensor
- **w** refers to continuous (water) phase
- **0** refers to surface of polymer particle or indicates initial
- **12** indicates relative motion
- **00** indicates at, infinity, saturation conditions, or undisturbed

**Dimensionless groups**

- **Fl** flow number, \( Fl = \frac{3\pi n c d E_{33}}{R_a} \)
- **Pd** polydispersity, \( Pd = \frac{\pi^{\frac{1}{2}} \mu_{\text{a}}}{\mu_{\text{i}}} \)
- **Pe** particle Péclet number, \( Pe = \frac{E_{33}^{\frac{1}{2}}}{D \omega} \)
- **Re\_L** Reynolds number of large energy-containing eddies, \( Re_L = \frac{\omega L}{\nu} \)
- **Re\_\lambda_s** Reynolds number at the Taylor microscale, \( Re_{\lambda_s} = \frac{\omega \lambda_s}{\nu} \)
- **Rp** repulsion number, \( Rp = \frac{\omega_{\lambda_s} e}{H_a} \)
- **RD** diffusivity ratio, \( RD = \frac{D_c \omega}{D_w} \)
Abbreviations
CFD computational fluid dynamics
CLM Clayfield, Lumb and Mackey
CMC critical micelle concentration
DLS dynamic light-scattering
DNS direct numerical simulation
DLVO Debye-Landau-Verwey-Overbeek
IHP inner Helmholtz plane
IR infrared
LDV laser Doppler velocimetry
OHP outer Helmholtz plane
PBE population balance equation
rms root mean square
SDS sodium dodecylsulphate
SEM scanning electron microscopy

Special
\( \vec{e}_s \) unit vector along the line connecting the centers of two particles
\( O(y) \) order of magnitude equal to \( y \)
\( r, \theta, \phi \) spherical coordinates in radial, tangential, and azimuthal direction
\( x_1, x_2, x_3 \) rectangular coordinates
\( \vec{x} \) indicates tensor quantity \( x \)
\( \dot{x} \) indicates dimensionless quantity \( x \)
\( x' \) indicates fluctuation of quantity \( x \)
\( \overline{x}, <x> \) indicates (ensemble) averaged quantity \( x \)
\( \vec{x} \) indicates vector quantity \( x \)
\( \delta_{j,k} \) Kronecker delta (\( \delta_{j,k} = 1 \) if \( j = k \), else \( \delta_{j,k} = 0 \))
\( \delta(m - m_0) \) Kronecker delta (\( \delta(m - m_0) = 1 \) if \( m = m_0 \), else \( \delta(m - m_0) = 0 \))
\( \Delta C_{e,\text{tot}} \) required change of the total emulsifier concentration to reach the inflection point (mol/m\(^3\)w)
\( \nabla \) gradient operator
\# indicates "number"
Curriculum vitae

born September 15, 1971

1977-1983 primary school in Zevenhuizen (the Netherlands)

1983-1989 gymnasium in Capelle aan den IJssel (the Netherlands)

1989-1995 studies in Chemical Engineering at Delft University of Technology (the Netherlands)


1994 research project in the group of Prof. J.R. Bourne (ETH Zürich), studying how turbulent mixing influences chemical reactions

1994-1995 research project "Simulation of the hydrodynamics of a bubble column." carried out at Syncrude Research (Edmonton, Canada) in collaboration with Prof. S.M. Kresta (University of Alberta)

1995 diploma work "The flow characteristics near the feed pipe in a (turbulent) tubular reactor.", in the group of Prof. H.E.A. van den Akker (Kramers Laboratorium voor Fysische Technologie), M.Sc.

1995-1996 project on integrated development of chemical processes in Prof. K. Hungerbühler's group (ETH Zürich, Laboratorium für Technische Chemie)

1996-1999 Ph.D.-project in the group of Prof. M. Morbidelli (ETH Zürich, Laboratorium für Technische Chemie)