Collodial stability measurement of polymer latices and their aggregation in agitated vessels

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Colloidal Stability Measurement of Polymer Latices and their Aggregation in Agitated Vessels

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Abstract

Emulsion polymerization represents a viable choice for the production of plastic materials due to its inherent thermal control, high productivity even for high molecular weights and moderate viscosity increases. The resulting product is a colloidal dispersion of polymeric particles in water usually called latex. An important advantage of such a product with respect to the bare polymer is that its colloidal character enables the use “as such” in many applications such as for example paints, coating and finishes. On the other hand, when the application requires the polymeric material in powder form, a process for separating the polymer from water has to be set up. In the most common case of electrostatically stabilized latices, the simplest processes to accomplish the separation of the dispersed polymer from water is that based on salt induced aggregation. Despite its apparent simplicity, much of the physics involved, such as the colloidal stability of latices stabilized by adsorbable ionic surfactants and the interplay between salt into latex mixing and aggregation at high polymer volume fraction, is not yet fully understood. This thesis tackles these issues and is accordingly divided in two parts. The first is devoted to the study of the colloidal stability of model latices. Here we propose a general methodology for the estimation of the doublet formation rate constant (proportional to the stability ratio of primary particles) in quiescent colloidal dispersions from measurements obtained by common optical techniques, such as dynamic light scattering, static light scattering (nephelometry) or turbidimetry. In contrast to previous approaches relying on the initial slopes of the measured quantities, such as the mean hydrodynamic radius, scattered light intensity or turbidity, we introduce a transformation of the measurables to properly scaled quantities, which grow linearly in time with a slope proportional to the doublet formation rate. Analysis of systematic and random errors allows one to control the error in the estimated value of the aggregation rate. Using this approach, we measure the aggregation rate constant of colloidal polymer particles prepared by surfactant-free emulsion copolymerization of styrene and 2-hydroxyethyl methacrylate (HEMA). We find that the stability ratio at constant ionic strength decreases with increasing dilution of the original polymer latex. This can be explained by the presence of non-reacted stabilizing species (most likely oxidized HEMA) that desorb
from the particle surface upon latex dilution and thus diminish the repulsive interactions between particles.

Then we use the proposed methodology for the measurement of doublet formation rate to investigate the colloidal stability of polystyrene latex particles stabilized with sodium dodecyl sulfate (SDS) under slowly aggregating conditions (stability ratio $W > 10^6$) at relatively high volume fractions ($\phi > 0.1$). We find that apparent surface charge densities, calculated from the measured aggregation rate constants by modeling interparticle interactions in a DLVO framework, increase strongly with increasing electrolyte concentration for all latices, contrary to the results from previous electrophoretic mobility measurements on the same system. Our data indicate that these highly charged latex particles in sodium chloride solutions repel each other stronger than expected from the classical diffuse double layer DLVO theory. The additional repulsion can be explained by postulating the presence of a repulsive term with a simple exponential decay in addition to the DLVO particle interaction energy. The additional repulsive interaction can be related to dipole-dipole interactions, dehydration of sodium surfactant counterions or steric repulsion between surfactant molecules upon the close approach of two aggregating particles. This extended DLVO approach should be considered as an empirical correction capable of explaining our experimental data on aggregation kinetics of highly charged polystyrene latexes.

In the second part of this thesis is concerned with the salt induced aggregation in flowing conditions at high polymer volume fractions. In order to use the focused beam reflectance measurement (FBRM) technique to measure particle size on-line in-situ, we start developing a model for particle detection in FBRM in the general case of particles of any convex shape. Shape dependent convolution relationships between measured chord length distribution (CLD), particle size distribution (PSD) and particle mass distribution (PMD) are then derived and an explicit formula for the weighting characteristic length is given in terms of particle shape. Based on the derived convolution relationships equations relating moments of the CLD, PSD and PMD are obtained. Issues related to the definition of particle size of non spherical objects and its connection to the particle sizing technique are discussed. Based on moment relationships, particle size is defined for FBRM measurements in terms of a CLD equivalent sphere. CLD and characteristic length for a thin cylinder are obtained analytically and used as simple model in order to illustrate issues in sizing particles of variable shape. General conclusions regarding the role of the weighting characteristic length in the behavior of the measured CLD are drawn.
Such modeling result enable us to take on the problem of the aggregation of latices in stirred vessels. We start with an assessment of the relative magnitude of the timescales of mixing and aggregation of fully destabilized polymeric latices in stirred vessels. We demonstrate that, in industrially relevant conditions (i.e. volume fractions above 10% and primary aggregate sizes below 200 nm), latices aggregate and possibly gel before complete mixing is achieved. By means of FBRM, we measure on-line and in-situ the size of aggregates obtained aggregating a PVDC latex at salt concentrations above the critical coagulation concentration in a stirred vessel operated in semibatch. Several experimental runs are conducted and averages of the aggregate size distribution, i.e. volume and number averages, are measured at various values of the feed flowrate, feed solid volume fraction, stirring speed and final volume fraction in the vessel. It is found that, at high feeding volume fractions, particles instantaneously aggregate and gel upon entering the vessel. Resulting aggregates are then broken down to volume weighted average sizes falling in the range between 100 and 400 microns at steady state. The experimental results are interpreted in terms of a competition between the aggregation/gelation process and mixing. In particular, by evaluating the relevant characteristic times, it is found that the process is dominated by the competition between mesomixing at the location where the latex enters the vessel and the aggregation/gelation process. Scanning electron micrographs of dry samples obtained after thermal treatment show aggregate morphologies which further support the above interpretation.
Riassunto

La polimerizzazione in emulsione rappresenta una scelta vantaggiosa per la produzione di materie plastiche a causa del facile controllo termico, della alta produttività anche ad alti pesi molecolari ed agli incrementi della viscosità moderati. Il prodotto risultante da un processo di polimerizzazione in emulsione è una dispersione colloidale costituita da particelle polimeriche che usualmente viene chiamato lattice polimerico. Un vantaggio importante di un tale prodotto risiede nel fatto che può essere utilizzato senza il bisogno di ulteriori lavorazioni in molte applicazioni come ad esempio nel caso di pitture, rivestimenti e finissaggi. D'altra parte, quando l'applicazione richiede l'utilizzo del materiale polimerico sotto forma di polvere, vi è la necessità di implementare un processo atto a separare il polimero disperso dall'acqua. Nel caso comune di lattici stabilizzati per via elettrostatica, il processo più semplice utile ad effettuare tale separazione è solitamente basato sull'aggregazione indotta da sale. Nonostante l'apparente semplicità di tale processo, una buona parte della fisica coinvolta, come ad esempio la stabilità colloidale di lattici stabilizzati da surfattanti ionici e l'interazione tra la miscelazione del sale nel lattice e l'aggregazione ad alte frazioni volumetriche di polimero, non ancora pienamente compresa. Questa tesi affronta tali problematiche ed è divisa in due parti. La prima è dedicata allo studio della stabilità colloidale di lattici modello. In essa viene proposta una metodologia generale finalizzata all calcolo della costante cinetica di formazione del doppietto (che risulta proporzionale al cosiddetto rapporto di stabilità delle particelle primarie) in dispersioni colloidali quiescenti attraverso misure ottenute tramite tecniche ottiche, quali ad esempio il light scattering dinamico, il light scattering statico e la turbidimetria. Contrariamente ad approcci precedenti riportati in letteratura basati sulla pendenza iniziale delle quantità misurate quali raggio idrodinamico, intensità di luce scatterata o turbidità, viene introdotta una trasformazione dei misurabili in quantità propriamente scalate, le quali crescono linearmente nel tempo e la cui pendenza risulta proporzionale alla costante cinetica di formazione del doppietto. L'analisi dell'errore sistematico e casuale ci premette di controllare l'errore nel valore calcolato della costante cinetica. Attraverso tale approccio veine misurata la costante cinetica di aggregazione di particelle polimeriche colloidali preparate attraverso una copolimerizzazione in emul-
sione di 2-idrossietilmetacrilato (HEMA) e stirne condotta in assenza di surfattante. Viene riscontrato che il rapporto di stabilità a forza ionica costante decresce al crescere della diluizione del lattice originale. Ciò può essere spiegato in base alla presenza di specie stabilizzanti non reagite (con buona probabilità una forma ossidata dell’HEMA) che desorbono dalla superficie delle particelle all’incrementare della diluizione, causando, in conseguenza, una diminuzione delle forze repulsive agenti tra le particelle. Di seguito tale metodologia viene applicata allo studio della stabilità colloidale di lattici polimerici stabilizzati attraverso sodio dodicilsolfato (SDS) in condizioni di aggregazione lenta (fattore di stabilità $W > 10^4$) a frazioni di volume solido relativamente elevate ($\phi > 0.1$). Viene mostrato che la densità superficiale di carica apparente, calcolata attraverso la modellazione delle forze interparticella nel quadro della teoria DLVO a partire dalle costanti cinetiche di aggregazione misurate, cresce marcatamente all’incrementare della forza ionica per tutti i lattici investigati, in contrasto con i risultati ottenuti mediante misure di mobilità elettroforetica condotti sui medesimi lattici. I nostri dati indicano che i lattici a carica superficiale in esame si repellono più fortemente rispetto alle previsioni della teoria DLVO del doppio strato diffuso in soluzioni di cloruro di sodio. Tale repulsione addizionale può essere spiegata postulando la presenza, oltre ai termini previsti dalla teoria DLVO, di un contributo repulsivo espresso attraverso un semplice termine a decadimento esponenziale. Tale termine aggiuntivo di repulsione può essere dovuto ad una interazione dipolo-dipolo, alla deidratazione degli ioni sodio oppure ad interazioni steriche tra molecole di surfattante che possono insorgere all’avvicinarsi di due particelle. Tale estensione della teoria DLVO è da considerarsi una correzione empirica capace di spiegare i nostri dati sperimentali relativi alla cinetica di aggregazione di lattici polimerici ad alta densità di carica superficiale.

Nella seconda parte di questa tesi si affronta la problematica relativa all’aggregazione indotta da sale in condizioni di flusso ed ad alte frazioni di massa solida. Al fine di utilizzare la tecnica denominata “focused beam reflectance measurement” (FBRM) per la misura della dimensione delle particelle in linea ed in situ, viene sviluppato un modello matematico relativo alla scansione delle particelle nella tecnica FBRM nel caso generale di particelle di forma convessa qualunque. In seguito le relazioni di convoluzione correlanti le distribuzioni di grandezza (PSD) di massa (PMD) e di corde (CLD) delle particelle vengono derivate insieme ad una formula esplicita per la dimensione peso caratteristica in funzione della forma della particella. Sulla base di tali risultati, le relazioni tra i vari momenti di tali distribuzione vengono ottenute. Ciò permette la definizione di una dimensione della particella ottenibile attraverso la tecnica FBRM in termini di una sfera.
equivalente CLD. Infine la CLD e la lunghezza caratteristica di un cilindro sottile vengono derivate analiticamente ed usate come modello al fine di illustrare le problematiche relative alla misura della grandezza di particelle di forma variabile.

I risultati modellistici di cui sopra ci permettono di affrontare la problematica dell’aggregazione di lattici in recipienti agitati. Innanzitutto un esame riguardante la grandezza relativa dei tempi caratteristici di mescolamento e aggregazione di lattici polimerici in condizioni di piena destabilizzazione in recipienti agitati viene presentata. Si dimostra che, in condizioni di rilevanza industriale (i.e. frazioni di volume solido al di sopra del 10% e dimensione al di sotto di 200 nm), i lattici aggregano a eventualmente gelano prima che un mescolamento completo sia stato raggiunto. Attraverso la tecnica FBRM, viene misurata la grandezza degli aggregati ottenuti tramite l’aggregazione di un lattice PVDC a concentrazioni di sale superiori alla concentrazione critica di coagulazione in un recipiente agitato operato in semibatch. Vari esperimenti sono condotti e le corrispondenti medie della distribuzione di grandezza degli aggregati misurate a differenti valori della portata volumetrica in ingresso, della frazione di volume solido, dell’intensità dell’agitazione e della frazione di volume solido finale. Si riscontra che, a frazioni di volume elevate, le particelle aggregano e gelano istantaneamente non appena entrano nel recipiente. Gli aggregati così formati vengono successivamente frammentati fino a raggiungere dimensioni medie in volume a stato stationario tra i 100 e 400 micron. Tali risultati sperimentali vengono in fine interpretati in relazione alla competizione tra il processo di aggregazione/gelazione ed il processo di mescolamento. Più in dettaglio, valutando i tempi caratteristici rilevanti, viene dimostrato che il processo è dominato dalla competizione tra mesomixing nella zona dove il lattice entra nel recipiente ed i processi di aggregazione/gelazione. Immagini di vari campioni secchi trattati termicamente, ottenute tramite un microscopio a scansione elettronica, mostrano morfologie di aggregati che confermano le interpretazioni precedenti.
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Particle number concentration \( N \) and surface area \( S \) refer to the latex volume. SDS concentration \( c_{s,aq} \) and ionic strength \( I \) refer to the aqueous phase volume. \( \gamma_0 \) and \( c_{s,aq} \) : calculated using the SDS adsorption isotherm. Scattering vector modulus \( q = 1.87 \times 10^7 \text{ m}^{-1} \); \( \lambda_0 = 632.8 \text{ nm} \). 50

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1 Introduction

1.1 Colloids in the Industry: Aim of the Work

Colloidal systems (or more simply colloids) refer to physical systems in which at least two phases are present one of which (the so called dispersed phase) is characterized by a characteristic size falling in the range between 1 nm and 1 μm. It is this scale, the so-called mesoscale, that distinguishes colloids from the macroscopic systems studied in the classical fields of physics (e.g. mechanics or hydrodynamics) and the microscopic systems, namely atoms and molecules, that are the subject of chemistry. Colloidal length-scales are large enough that quantum effects, typical of atoms and molecules, do not play a role and that the interaction of colloidal particles with the molecules constituting the dispersing medium can be accounted for in an averaged way typical of continuous mechanics. On the other hand, colloidal particles are small enough to exhibit thermal motion. If one considers values of density typical organic solid or liquid substances and evaluates the relative importance of thermal motion versus macroscopic body forces (e.g. gravitational forces) he will found out that 1 μm is the critical size beyond which macroscopic forces start to predominate. The fact that colloidal length-scales happen to be sufficiently large to permit a relatively easy characterization, by means for example of neutron or light scattering, and small enough so that a statistical approach in the description of their physical behaviour is feasible, has made colloidal system a fruitful playground for physicists to test their theories. On the other hand, the peculiar characteristics of colloidal systems confer them properties of technological relevance. As a result colloids are ubiquitous in industry, soaps, inks, glues, dairy products such as milk and yoghurt and foams being some examples. An example of how features typical of colloidal systems can be profitably exploited in industry is that given by emulsion polymerization [4, 5]. In the production of plastic materials bulk polymerization refers to the situation where the liquid monomer is polymerized without the use of a solvent. Due to the exothermic character of polymerization reactions, bulk polymerization is seldom implemented and polymerization in solution is preferred. The addition of an inert
solvent on one side lowers concentration thus slowing down the polymerization kinetics, on the other hand it also lowers the heat produced per unit time and per unit mass. Polymerization in solution, however, introduces the problem of separating the polymer from the solvent and end lowers the productivity of the process. In many situations of practical interest a better solution can be implemented by adopting emulsion polymerization. Typically, an emulsion of the monomer in water is prepared by adding a surface active molecule. In this way a colloidal system of monomer in water is obtained. Due to extraordinary large inter-phase surface between monomer and water characteristic of the emulsion (and of colloids in general), when a water soluble initiator is introduced and polymerization starts, monomer molecules rapidly diffuse out of the monomer phase to reach the growing chains. In the early stages of this process the growing chains reach a critical size where they collapse to form a new dispersed phase where the polymerization continues as monomer keeps diffusing through the dispersing phase so as to reach the reacting chains. In the same time the heat produced in the reacting phase, again thanks to the large specific surfaces, is distributed over the entire system. Due to the large heat capacities of water, the resulting temperature increases are smaller then the case of solution polymerization thus allowing for a better temperature control. At the end of the polymerization reactor a dispersion in water of polymeric particles (usually called latex) of sizes typically in the range of 30 nm to 500 nm is obtained. In this example we have seen how a feature typical of colloidal systems, i.e. extremely large specific surfaces, plays a fundamental role in the development of an industrial process.

Since, as illustrated above, colloidal particles move thermally they are likely to collide and stick together due to interparticle attractive dispersion forces. This physical process, known as aggregation, results in an increase in size that ultimately leads to phase separation and loss of the colloidal character. It is then clear that repulsion forces must exist to prevent such phenomenon so as to ensure a suitable shelf-life to the latex. Actually, even in the presence of such a stabilization mechanism, a finite probability of successful collision still exists. However, such an event can be so unlikely that latices can practically exhibit indefinite shelf-life. As an example, colloidal gold dispersions prepared by Michael Faraday over one century ago [6] are still conserved nowadays in the Museum at The Royal Institute in London, England. Colloidal dispersions are consequently said to be kinetically stable as opposed to thermodynamically stable. Coming back to the example of the preparation polymeric latices, we now understand that the ionic amphiphilic molecules used for the preparation of the initial monomer emulsion will adsorb on the surface of the particles, consequently developing a surface charge...
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that will cause the particles to repel each other and provide colloidal stability. On the
other hand, in such systems, aggregation can be purposely induced by adding a strong
electrolyte to the system which will screen the surface charge, consequently lowering the
repulsion forces and allowing the aggregation of particles on observable timescales. The
electrolyte concentration can be increased until reaching the so-called critical coagula-
tion concentration (CCC) beyond which repulsion forces are completely screened and
the rate of aggregation reaches a plateau. Colloidal aggregation has been extensively
studied in the scientific literature ever since the first seminal work of Marian von Smolu-
chowski appeared between years 1916 and 1917 [7, 8]. There he studied the mutual
diffusion of particle pairs and, assuming instantaneous aggregation upon contact, he
was able to derive the rate equation for the particle aggregation in absence of repul-
sion forces. Adopting a similar approach Fuchs [9] introduced interparticle forces and
derived a similar rate equation where the rate constant is expressed as the ratio of the
rate constant in absence of repulsion forces, as derived by Smoluchowski, to the so called
Fuchs' stability ratio $W$. It wasn't until the forties that two group of scientists Derjaguin
and Landau [10] and Verwey and Overbeek [11] independently provided models for the
dispersion and electrostatic forces to be used in the framework of Fuchs' theory, thus
giving rise to what is called today the DLVO theory.

Apart from the scientific interest about colloidal aggregation as physical phenomenon
per se, aggregation can be a useful tool for separating the colloidal particles from the
dispersing phase. Indeed in the production of polymeric latices it is often desirable to
obtain the plastic material in powder from. To this end a latex is mixed with a salt
solution to induce aggregation and therefore cause the plastic material to sediment.
Accordingly, a typical industrial process for separating the polymer phase from water in
an electrostatically stabilized latex is based on mixing a salt solution with the latex in
an agitated vessel operated in batch or continuous mode. It is commonly chosen to work
in fully destabilized conditions, i.e. at salt concentrations above CCC, in order to avoid
the strong dependency of the aggregation rate upon salt concentration, consequently
favoring the productivity and the robustness of the process. In these conditions, the
aggregation process becomes very fast thus competing with the mixing process typical
of stirred vessels, and leading to gels even in the presence of substantial breakage. The
complex interplay among these processes is not investigated in the literature covering
salt induced aggregation of electrostatically stabilized latices in agitated vessels [12–20],
where the aggregation process is significantly slowed down by operating at extremely
low particle volume fractions. In addition, the particle size of the latices used in the
aggregation experiments was normally above 1 μm, which is far bigger than the particle sizes in typical industrial latices, which are of the order of hundred nanometers.

The main topic of this thesis will be focused on these issues. In Chapter 5 results from suitable experiments in a stirred vessel with fully destabilized latices of a small particle size in concentrated conditions, which are the conditions typical of industrial applications, are presented. By monitoring on-line and in-situ the time evolution of the size distribution of the polymer aggregate dispersion, information about the competition between aggregation, breakage and the mixing processes can be obtained. The monitoring device of choice will be based on the focused beam reflectance principle, which allows for on-line/in-situ measurements at solid volume fractions up to 40%. In Chapter 4 we develop a novel mathematical model for the particle detection in focused beam reflectance measurement (FBRM) which allows for a correct interpretation of measured data in terms of average sizes in the system. Due to the aforementioned requirement of operating at salt concentrations above the CCC, Chapter 2 will be devoted to the development an experimental methodology which allows a convenient estimation of the CCC. Accordingly to the measurement of the initial primary particle aggregation rate by means of light scattering techniques which are commonly available in experimental laboratories will be studied. The required light scattering background is presented in the remaining section of this introduction. In Chapter 3 such technique will be used to assess the applicability of the DLVO theory to the description of the colloidal stability of model electrostatically stabilized latex.

1.2 Light Scattering by Colloidal Dispersions

The scattering of light represents the experimental technique of choice for the characterization of colloidal dispersions. In a light scattering experiment monochromatic light emitted by a laser passes through a polarizer and illuminates a volume V in the sample. The scattered light is polarized and eventually hits a detector placed at a distance $R_d$ that records the impinging light intensity. This is illustrated in Fig. 1.1. Within this description, and assuming the medium to be nonmagnetic and nonadsorbing with

1In reality, in the modern implementations, the measured quantity is the number of photons hitting the detector per unit time (normally expressed in kilo counts per second) instead of light intensity. A simple linear relationship, which involves the quantum efficiency of the used photocathode, connects the photocount rate to the light intensity. Nevertheless this distinction is immaterial to our description and for sake of simplicity we will disregard any detail about technical implementations.
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Figure 1.1: A schematic representation of a light scattering experiment.

an average refractive index \( n_s = \sqrt{\varepsilon_s} \) where \( \varepsilon_s \) is the dielectric constant, the incident electric field is a planar wave and can be expressed as

\[
E_i(r, t) = \hat{n}_i E_0 \exp(k_i \cdot r - \omega_i t),
\]

where \( \hat{n}_i \), the polarization vector, is a unit vector with orientation and direction of the incident electric field, \( E_0 \) is the field amplitude, \( k_i \), the so-called propagation vector, is a vector with a direction parallel to the propagation of the incident light and magnitude \( k_i = 2\pi n_s/\lambda_0 \) with \( \lambda_0 \) the wavelength of the incident light in vacuo and \( \omega_i \) is the angular frequency. When such wave encounters an infinitesimal optically isotropic colloidal particle of volume \( d^3 r \), dielectric constant \( \varepsilon_p = \varepsilon_s + \delta \varepsilon \) and characteristic size much smaller than \( \lambda_0 \), the far-field scattered electric field at a distance \( R_d \gg \sqrt[3]{V} \) from the scattering volume is [21]

\[
E_s(R, t) = \frac{E_0 k^2_f}{4\pi R_d \varepsilon_s} \exp(ik_f R_d) \exp[i(q \cdot r - \omega_i t)]\hat{e} \delta \varepsilon \ d^3 r, \tag{1.1}
\]

here \( k_f \) is the scattered propagation vectors, \( q \) is the scattering vector defined as

\[ q \equiv k_i - k_f, \]

and the unit vector \( \hat{e} \) is defined as

\[
\hat{e} = \frac{k_f \times k_f \times \hat{n}_i}{k_f^2}.
\]
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If a polarizer with polarization $\hat{\mathbf{n}}_f$ were present between the scattering volume and the detector, the module of the scattered electric field at the detector would read

$$E_s(R,t) = \frac{E_0k_f^2}{4\pi R_dC_0} \exp(ik_fR_d) \exp[i(q \cdot r - \omega_t)] \hat{\mathbf{n}}_f \cdot \hat{\mathbf{e}} \delta \epsilon d^3r.$$  \hspace{1cm} (1.2)

If the colloidal particle is non adsorbing, no energy from the incident light is transferred to the particle in the scattering event. Consequently, the scattered light has the same energy of the incident light and we can write

$$k_i = k_f.$$  

Under this assumption we limit ourself to what is usually referred to as elastic light scattering.

To proceed further it is useful to provide some definitions concerning the scattering geometry. The scattering plane is defined as the plane formed by the incident and scattered light propagation vectors, while the scattering angle is the angle $\theta$ between the two. It follows that the module $q$ of the scattering vector can be written in terms of the scattering angle as

$$q = \frac{4\pi n_g}{\lambda_0} \sin(\theta/2).$$

If we set up a Cartesian coordinate system $Oxyz$ with base $\{i, j, k\}$ such that the $y$-axis has the direction and orientation of $k_i$, the $xy$-plane coincides with the scattering plane and $\hat{k}$ has direction and orientation of $k_f \times k_i$ as illustrated in Fig. 1.2, the unit vector $\hat{\mathbf{e}}$ can be then expressed as

$$\hat{\mathbf{e}} = \cos^2 \theta \cos \phi \hat{i} + \sin \theta \cos \theta \cos \phi \hat{j} + \sin \phi \hat{k},$$

where $\phi$ is the angle between the incident light polarization vector, $\hat{\mathbf{n}}_i$ (see Fig. 1.3(a)). Furthermore, by defining $\psi$ as the angle formed by the scattered light polarization vector with the scattering plane (see Fig. 1.3(b)), $\hat{\mathbf{n}}_f$ can be calculated as (see Fig. 1.3(c))

$$\hat{\mathbf{n}}_f = \sin \psi \hat{k} + \cos \psi (\cos \theta \hat{i} - \sin \theta \hat{j}).$$

The formula above eventually enable us to write the term $\hat{\mathbf{n}}_f \cdot \hat{\mathbf{e}}$ appearing in Eq. (1.2)
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Figure 1.2: Illustration of the scattering geometry.

Figure 1.3: Definition of the scattering angles.
\[ \hat{n}_f \cdot \hat{e} = \cos \psi \cos \theta \cos \phi (\cos^2 \theta - \sin^2 \theta) - \sin \psi \sin \phi. \]  

(1.3)

In any real situation our sample will contain more than one particle, in addition the limitation on the particle size required for the treatment above seems too restrictive. In order to overcome these limitations, within the so-called Rayleigh-Debye approximation, the contribution of each elementary volume, as given by Eq. (1.1) (or equivalently Eq. (1.2)), is summed up over all the infinitesimal volumes constituting the colloidal particles comprised in the scattering volume. This approach is accurate only if the incident light, due to the presence of the other volumes within the particle, has not experienced a substantial phase shift before reaching the elementary volume, thus allowing the aforementioned summation [22]. This is equivalent to the requirement that the phase shift caused by the presence of a particle of characteristic size \( a \) be small, i.e.

\[ 2\pi |n_p - n_s| \frac{a}{\lambda_0} \ll 1. \]

It is clear then that, if the colloidal particles possess a refractive index similar to that of the suspending medium, the present approach will be valid for particle sizes larger than those in the previous approximation. It should be noted, though, that within the Rayleigh-Debye approximation the particle concentration must be low enough to avoid multiple scattering, that is to say to avoid that a wavelet scattered by a certain particle hits another particle before reaching the detector. Under these assumptions Eqs. (1.4) and Eq. (1.5)) become

\[ E_s(R, t) = \frac{E_0 k_f^2}{4\pi R_d \varepsilon_s} \exp(i k_f R_d - \omega i t) \hat{n} \delta \varepsilon(q, t), \]  

(1.4)

and

\[ E_s(R, t) = \frac{E_0 k_f^2}{4\pi R_d \varepsilon_s} \exp(i k_f R_d - \omega i t) \hat{n}_f \cdot \hat{e} \delta \varepsilon(q, t). \]  

(1.5)

respectively, where \( \delta \varepsilon(q, t) \) is the following spatial Fourier transform of the dielectric constant difference:

\[ \delta \varepsilon(q, t) \equiv \delta \varepsilon \int_V d^3r \exp(iq \cdot r)\rho(r, t), \]  

(1.6)
here \( \rho(r,t) \) is equal to 1 whenever \( r \) falls within a particle and zero otherwise.

### 1.2.1 Static Light Scattering

In a static light scattering experiment (SLS) the time averaged scattered light intensity, \( I_f \), is measured at different scattering angles. The collected data will contain information about the average particle size of the colloidal dispersion under exam, which can be extracted by means of a further development of the modeling framework illustrated in the previous section.

For seek of simplicity let us restrict ourselves to the situation where the colloidal dispersion at hand is constituted by monodisperse spherical primary particles of radius \( R \). Since in this thesis we are studying aggregation phenomena, we include the situation where aggregates of such a monodisperse population of primary particles are present. We assume also that the primary particles contained in the aggregates retain their spherical shape. Starting from Eq. (1.5) we can write the following expression for \( I_f \)

\[
I_f = \langle E_s(R,t) E_s^*(R,t) \rangle = \frac{I_0 k_f^4}{16 \pi^2 R_d^2 \delta_s} \hat{n}_f \cdot \hat{e} \langle \delta e(q,t) \delta e^*(q,t) \rangle, \tag{1.7}
\]

where \( I_0 = E_0^2 \) is the incident light intensity and the superscript \( * \) denotes the complex conjugate. Since we assume the system to be at equilibrium, in the equation above we made use of the ergodic theorem \[23\] whereby the time average has been substituted by the ensemble average \( \langle \cdot \rangle \).

In Eq. (1.7) the only term needing further treatment is \( \langle \delta e(q,t) \delta e^*(q,t) \rangle \). By defining the function \( f(r') \) as

\[
f(r') = \begin{cases} 
1 & \forall \ r' : |r'| \leq 1 \\
0 & \forall \ r' : |r'| > 1 
\end{cases},
\]

the function \( \rho(r) \) can be rewritten as

\[
\rho(r) = \sum_j f(r - r_j),
\]

where \( r_j \) is the position of the centre of the \( j \)-th primary particle and the summation is
on all the primary particles. Performing the substitution \( \mathbf{r} = \mathbf{r}_j + \mathbf{r}' \) we can write

\[
\frac{\langle \delta \epsilon(q,t) \delta \epsilon^*(q,t) \rangle}{\delta \epsilon^2} = \left\langle \left[ \int_V d^3r \, e^{i\mathbf{q} \cdot \mathbf{r}} \sum_j f(\mathbf{r} - \mathbf{r}_j) \right] \left[ \int_V d^3r \, e^{-i\mathbf{q} \cdot \mathbf{r}} \sum_k f(\mathbf{r} - \mathbf{r}_k) \right] \right\rangle,
\]

\[
= \left\langle \sum_j e^{i\mathbf{q} \cdot \mathbf{r}_j} \sum_k e^{-i\mathbf{q} \cdot \mathbf{r}_k} \right\rangle \left[ \int_V d^3r' \, e^{i\mathbf{q} \cdot \mathbf{r}'} f(\mathbf{r}') \right]^2,
\]

\[
= P(q) \left\langle \sum_j e^{i\mathbf{q} \cdot \mathbf{r}_j} \sum_k e^{-i\mathbf{q} \cdot \mathbf{r}_k} \right\rangle,
\]

(1.8)

where we introduced the definition of the primary particle form factor \( P(q) \) as

\[
P(q) = \left[ \int_V d^3r' \, e^{i\mathbf{q} \cdot \mathbf{r}'} f(\mathbf{r}') \right]^2 = \left[ \frac{\sin(Rq) - Rq \cos(Rq)}{(Rq)^3} \right]^2.
\]

(1.9)

Having factored out the shape of the primary particle, we are left with studying the interference pattern due to the positioning of the centers of mass of the primary particles. Such an information is contained in the term in angle brackets appearing on the right hand side of the last equation in (1.8). Let us introduce \( \delta_{ij} \equiv \mathbf{r}_j - \mathbf{r}_i \) and \( \delta_{nm} \equiv \mathbf{r}_k - \mathbf{r}_n \) as the position of the \( i \)-th particle in the \( i \)-th aggregate and the position of the \( m \)-th particle in the \( n \)-th aggregate, respectively, both relative to the centers of mass \( \mathbf{r}_i \) and \( \mathbf{r}_n \) of the aggregates so that we can write

\[
\left\langle \sum_j e^{i\mathbf{q} \cdot \mathbf{r}_j} \sum_k e^{-i\mathbf{q} \cdot \mathbf{r}_k} \right\rangle = \left\langle \sum_{i=1}^{N_c} \sum_{n=1}^{N_a} \sum_{l=1}^{N_i} \sum_{m=1}^{N_n} e^{i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_n)} e^{i\mathbf{q} \cdot (\mathbf{r}_l - \mathbf{r}_m)} \right\rangle
\]

where \( N_c, N_i \) and \( N_n \) are the total number of aggregates, primary particles in the \( i \)-th aggregate and \( n \)-th aggregate, respectively. It is reasonable to assume that, in dilute conditions as those required by a light scattering experiment, the aggregate positions \( \mathbf{r}_i \) and \( \mathbf{r}_n \) be statistically independent. As a result in the equation above all the terms \( \exp(i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_n)) \) with \( n \neq i \) drop out and we can write

\[
\left\langle \sum_j e^{i\mathbf{q} \cdot \mathbf{r}_j} \sum_k e^{-i\mathbf{q} \cdot \mathbf{r}_k} \right\rangle = \sum_{i=1}^{N_i} \sum_{l=1}^{N_i} \sum_{m=1}^{N_n} e^{i\mathbf{q} \cdot (\delta_{il} - \delta_{lm})}.
\]

(1.10)

In order to simplify the notation it is convenient to group the contribution from aggregates containing the same number of primary particles. To achieve this let us use the number of primary particles \( i \) within an aggregate to identify the corresponding class
of aggregates and call \( N_t \) its number concentration. The expression above can be then written as

\[
\left\langle \sum_j e^{i\mathbf{q} \cdot \mathbf{r}_j} \sum_k e^{-i\mathbf{q} \cdot \mathbf{r}_k} \right\rangle = \sum_i V N_t i^2 S_i(q),
\]

where we have defined the structure factor of the aggregate containing \( i \) primary particles as

\[
S_i(q) = \frac{\left\langle \sum_{l=1}^{N_i} \sum_{m=1}^{N_i} e^{i\mathbf{q} \cdot (\mathbf{r}_l - \mathbf{r}_m)} \right\rangle}{i^2}.
\]

Defining the average structure factor \( S_Z(q) \) as

\[
S_Z(q) = \frac{\sum_i i^2 S_i(q) N_i}{\sum_i i^2 N_i},
\]

and substituting the calculated terms back into Eq. (1.7) we obtain the following expression for the scattered intensity

\[
I_f = \frac{I_0 k_f^4}{16\pi^2 R_2^2} \frac{\delta}{\epsilon} (\mathbf{n}_f \cdot \mathbf{e}) VN_t \langle i^2 \rangle S_z(q) P(q),
\]

here \( N_t \) is the total number concentration of aggregate in the system and \( \langle i^2 \rangle \) is defined as

\[
\langle i^2 \rangle = \frac{\sum_i i^2 N_i}{\sum_i N_i}.
\]

If we introduce the pair correlation function \( g_i(r) \) normalized to \( i - 1 \) within the \( i \)-fold aggregate the corresponding structure factor can be written as

\[
S_i(q) = i^{-1} \left( 1 + \int g_i(r) e^{iqr} d^3r \right)
= i^{-1} \left( 1 + \int_0^{\infty} 4\pi r^2 g_i(r) \frac{\sin(qr)}{qr} dr \right).
\]

For small \( qr \) the term \( \sin(qr)/(qr) \) can be expanded as

\[
\frac{\sin(qr)}{qr} = 1 - \frac{q^2 r^2}{6} + O(q^3 r^3)
\]
which substituted in the formula above for the structure factor gives

$$S_i(q) = 1 - \frac{q^2}{6} \int_0^\infty 4\pi r^2 g_i(r)r^2dr + O(q^3) = 1 - \frac{q^2R_{g,i}^2}{6} + O(q^3),$$  \hspace{1cm} (1.19)

where we have introduced the so called optical radius of gyration, $R_{g,i}$ defined as

$$R_{g,i} = \sqrt{\frac{\int_0^\infty 4\pi r^2 g_i(r)r^2dr}{\int_0^\infty 4\pi r^2 g_i(r)dr}} = \sqrt{\frac{\int_0^\infty 4\pi r^2 g_i(r)r^2dr}{i-1}} \approx \sqrt{\frac{\int_0^\infty 4\pi r^2 g_i(r)r^2dr}{i}}. \hspace{1cm} (1.20)$$

This result suggests that from the plot of intensity versus $q^2$ one is in principle able to determine the radius of gyration from the slope at low angles. However, real systems are polydisperse, consequently such a value will be an average radius of gyration, $\langle R_g \rangle$ over the whole aggregate population. In order to determine the proper weighting used to compute the contribution of each population, the approximate expression for the structure factor of the $i$-fold aggregate given in Eq. (1.19) must be substituted into the formula for the scattered intensity given in Eq. (1.15), the result being

$$I_f = \frac{I_0 k^4}{16\pi^2R_g^2} \frac{\delta \varepsilon^2}{\varepsilon_s^2} (\vec{n}_f \cdot \vec{e}) VN_i \langle i^2 \rangle \left( 1 - \frac{q^2}{6} \sum \frac{i^2 N_i R_{g,i}^2}{\sum N_i i^2} \right) P(q). \hspace{1cm} (1.21)$$

This shows that the following expression for the average radius of gyration holds true

$$\langle R_g \rangle = \sqrt{\frac{\sum i^2 N_i R_{g,i}^2}{\sum i^2 N_i}}. \hspace{1cm} (1.22)$$

Experiments show however that, plotting $\ln(I_f)$ versus $q^2$ (the so-called Guinier plot) yields a somehow extended interval of linearity at low $q$. This plot corresponds to the following Guinier approximation of the average structure factor

$$S_\varepsilon(q) \approx \exp \left[ -\frac{q^2 \langle R_g \rangle^2}{3} \right], \hspace{1cm} (1.23)$$

whose Maclaurin series of order 2 coincides with that appearing in Eq. (1.21).

\textbf{1.2.2 Dynamic Light Scattering}

In a dynamic light scattering experiment (DLS) the time evolution of the measured scattered light intensity is recorded. When the illuminated volume contains a colloidal
dispersion, the Brownian motion of the particles causes a change of the interference pattern which in turn results in an erratic fluctuation of the measured scattered light intensity. As a consequence, an analysis of the correlation in time of the scattered intensity should provide information about the diffusivity of the Brownian scatterers contained in the sample. This can be achieved by coupling the Rayleigh-Debye theory of light scattering illustrated before with the theory of Brownian motion of colloidal particles, ultimately providing information about the hydrodynamic size of the particles contained in the system. To this end let us start to write the definition for the measured scattered intensity autocorrelation function, \( g^{(2)} \):

\[
g^{(2)}(q, \tau) \equiv \frac{\langle I_f(q,t)I_f(q,t + \tau) \rangle}{I_f^2} = \frac{\langle E_f(q,t)E_f^*(q,t)E_f^*(q,t + \tau)E_f(q,t + \tau) \rangle}{I_f^2},
\]

where \( \tau \) is the correlation time. Since the system is at equilibrium we have dropped the dependence on the time \( t \) which is hereafter set to zero. Within the assumption that each scattered electric field in Eq. (1.24) is a Gaussian stochastic variable, the Wick’s theorem [24] allows us to express the four point ensemble average as a sum of products of two-point averages as follows

\[
g^{(2)}(q, \tau) = \frac{\langle E_f(q,0)E_f^*(q,0) \rangle \langle E_f(q,\tau)E_f^*(q,\tau) \rangle}{\langle E_f(q,0)E_f^*(q,0) \rangle^2} + \frac{\langle E_f(q,0)E_f(q,\tau) \rangle \langle E_f^*(q,0)E_f^*(q,\tau) \rangle}{\langle E_f(q,0)E_f^*(q,0) \rangle^2}
+ \frac{\langle |E_f(q,0)E_f^*(q,\tau)| \rangle \langle |E_f^*(q,0)E_f(q,\tau)| \rangle}{\langle E_f(q,0)E_f^*(q,0) \rangle^2}.
\]

The first of these term is equal to 1 for non-interacting aggregates, the second can be demonstrated to be equal to zero [24] while the third is equal \( |g^{(1)}(q, \tau)|^2 \) where the electric field auto-correlation function is defined as

\[
g^{(1)}(q, \tau) = \frac{\langle E_f(q,0)E_f(q,\tau) \rangle}{\langle E_f(q,0)E_f^*(q,0) \rangle}.
\]

Eq. (1.25) then becomes

\[
g^{(2)}(q, \tau) = 1 + |g^{(1)}(q, \tau)|^2,
\]

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which is known as Siegert relation. In real light scattering setups, however, the finite size of the detection area and the finite duration of the time interval over which photons are counted will cause the following modification of the relationship above [25]

\[ g^{(2)}(\mathbf{q}, \tau) = 1 + A' \left| g^{(1)}(\mathbf{q}, \tau) \right|^2, \]

with \( A' \) an optical constant of order one that is fitted experimentally.

To proceed further a suitable expression for the electric field auto-correlation function \( g^{(1)}(\mathbf{q}, \tau) \) has to be sought. By means of Eqs. (1.5) and (1.7) Eq. (1.26) becomes

\[ |g^{(1)}(\mathbf{q}, \tau)| = \left| \frac{\langle \delta \varepsilon(\mathbf{q},0) \delta \varepsilon^*(\mathbf{q}, \tau) \rangle}{\langle \delta \varepsilon(\mathbf{q},0) \delta \varepsilon^*(\mathbf{q},0) \rangle} \right|. \]

Applying the same procedure used in the previous section to factor out the internal interference pattern of the primary particles and aggregate we obtain

\[ |g^{(1)}(\mathbf{q}, \tau)| = \frac{\sum_i V N_i r_i^2 S_i(q)}{\sum_i V N_i r_i^2 S_i(q)} |g^{(1)}_i(\mathbf{q}, \tau)|, \]

with the scattered electric field autocorrelation function of the \( i \)-fold aggregate defined as

\[ |g^{(1)}_i(\mathbf{q}, \tau)| = \left| \langle e^{i q(\mathbf{r}_i(0)-\mathbf{r}_i(\tau))} \rangle \right|, \]

where \( \mathbf{r}_i \) is the position of the center of mass of the \( i \)-fold aggregate. In the equation above the contribution due to the rotational motion of the aggregates has been neglected. This is a strong approximation which loses validity for large primary particles or aggregates compared to \( q^{-1} \). Consequently, in the case of aggregating colloidal system this approach is strictly applicable for small primary particles and in the early stages of the aggregation process. Let \( P(\mathbf{r}, t = \tau | \mathbf{r}_0, t = 0) \) denote the conditional probability density function (PDF) that the \( i \)-fold aggregate is at position \( \mathbf{r} \) at time \( \tau \) given that at time zero it is placed at \( \mathbf{r}_0 \) and \( P(\mathbf{r}_0) = 1/V \) the probability of placing a particle at \( \mathbf{r}_0 \) in the scattering volume. Then the scattered electric field autocorrelation function for the \( i \)-fold aggregate

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is expressed as

\[
g_{i}^{(1)}(q, \tau) = \int d^3 r_0 P(r_0) \int d^3 r P(r, t = \tau | r_0, t = 0) \exp[-i q \cdot (r - r_0)],
\]

\[
= \int d^3 r P(r, t = \tau | r_0, t = 0) \exp[-i q \cdot (r - r_0)].
\]

(1.32)

From the theory of diffusion we know that, in dilute conditions, the conditional PDF reads

\[
P(r, t = \tau | r_0, t = 0) = \frac{1}{(4\pi D_i \tau)^{3/2}} \exp \left[ -\frac{|r - r_0|^2}{4D_i \tau} \right],
\]

(1.33)

where \(D_i\) is the diffusion coefficient of the \(i\)-fold aggregate. Substituting in Eq. (1.32) and solving the integral we obtain

\[
|g_{i}^{(1)}(q, \tau)| = \exp[-D_i q^2 \tau],
\]

(1.34)

which in turn allows us to finally write Eq. (1.30) as

\[
|g^{(1)}(q, \tau)| = \frac{\sum_i N_i i^2 S_i(q) \exp[-D_i q^2 \tau]}{\sum_i N_i i^2 S_i(q)}.
\]

(1.35)

The quantity \(D_i q^2\) has the dimensions of the inverse of time and it is customarily termed decay rate \(\Gamma_i\) [26,27], we then write

\[
|g^{(1)}(q, \tau)| = \frac{\sum_i N_i i^2 S_i(q) \exp[-\Gamma_i \tau]}{\sum_i N_i i^2 S_i(q)}.
\]

(1.36)

Thus, once \(|g^{(1)}(\tau)|\) is obtained from the experimentally measured intensity correlation function, through the previous relationships, useful information about particle diffusivities can be extracted by means of the method of cumulants [28]. The following MacLaurin expansion of \(h(-\tau) \equiv \ln |g^{(1)}(\tau)|\)

\[
h(-\tau) = K_1(-\tau) + K_2 \frac{(-\tau)^2}{2!} + K_3 \frac{(-\tau)^3}{3!} + \ldots
\]

(1.37)

defines the \(m\)-th cumulant \(K_m\) as \(d^m h(-\tau)/d(-\tau)^m\) evaluated at \(\tau = 0\). The most sensible information is contained in the first two terms \(K_1\) and \(K_2\): the latter is related to the polydispersity of the particle size distribution, while the first one, calculated from the initial slope of the plot \(\ln |g^{(1)}(\tau)|\) versus \(-\tau\), represents the average decay rate.
weighted by $G_i$

$$K_1 = \sum_i \frac{i^2 S_i(q) N_i(t) \Gamma_i}{\sum_i i^2 S_i(q) N_i(t)}$$

(1.38)

By dividing both terms by $q^2$ we obtain the intensity weighted average of the diffusion coefficient

$$\bar{D} = \frac{\Gamma}{q^2} = \frac{\sum_i i^2 S_i(q) N_i(t) D_i}{\sum_i i^2 S_i(q) N_i(t)}.$$  

(1.39)

Often reported result of DLS measurements is the mean hydrodynamic radius resulting from the application of the Stokes-Einstein equation to the mean diffusivity

$$R_{DLS}(t, q) \equiv \frac{kT}{6\pi \mu D} = \frac{i^2 S_i(q) N_i(t)}{\sum_i i^2 S_i(q) N_i(t)/R_i^H},$$

(1.40)

where $R_i^H \equiv kT/(6\pi \mu D_i)$ is the hydrodynamic radius of the $i$-fold aggregate. The equation shows that at the beginning of the aggregation process, where only a monodisperse population of primary particle is present, $R_{DLS}(0, q) = R_i^H = R$. Finally it is worth noting that $R_{DLS}$ and $R_i^H$ are simply radii of spheres whose diffusion coefficient is, in diluted conditions, equal to the average diffusivity $\bar{D}$, and the diffusivity of the $i$-fold cluster $D_i$, respectively. Only in the special case when all aggregates are spherical, e.g. due to coalescence, Eq. (1.40) can be rewritten in terms of the aggregate radii $R_i = R_i^H$, so that for $q \ll 1/\max\{R_i\}$ (i.e. point scatterers) $R_{DLS}$ reduces to the following average radius

$$R_{DLS}(t) = R_{DLS}(t) = \frac{\sum_i N_i(t) R_i^6}{\sum_i N_i(t) R_i^6},$$

(1.41)

1.3 Turbidity

In turbidimetry the intensity $I_i$ of the light transmitted by an incoherent monochromatic light beam impinging the sample is measured. Turbidity, which physically represents the sum of scattered and absorbed power per unit volume and unit intensity of incident light, is then calculated through the relationship

$$\gamma = \frac{\log(I_0/I_i)}{l},$$

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where \( l \) is the length of the path traveled by the incident light. Turbidity can be related to the cluster number concentrations \( N_i \) through the total extinction cross-sections \( \sigma_i \), which are defined as the power absorbed and scattered by the single cluster per unit intensity of incident light. Indeed, based on such definition, we can write the following balance on the transmitted light intensity \( I \)

\[
\frac{dI}{dx} = - \sum_i N_i \sigma_i I,
\]

where \( x \) is the coordinate in the transmission direction. Its trivial solution, with boundary conditions \( I(0) = I_0 \) and \( I(l) = I_t \), leads to

\[
\gamma(t) = \sum_i N_i(t) \sigma_i.
\]  

Consequently the problem is reduced to that of calculating \( \sigma_i \). To this end let us introduce the differential scattering cross-section \( d\sigma_i/d\Omega \) of the \( i \)-fold aggregate defined as the power absorbed and scattered by the single cluster per unit intensity of incident light and unit solid angle \( \Omega \):

\[
\frac{d\sigma_i}{d\Omega} = \frac{\bar{I}_{f,i} dS}{I_0} = \frac{\bar{I}_{f,i} R_d^2}{I_0},
\]

here \( \bar{I}_{f,i} \) is the scattered intensity from the \( i \)-fold cluster, \( dS \) is the differential surface placed at a distance \( R_d \) from the scattering sample subtending the differential solid angle \( d\Omega \) and the term \( \bar{I}_{f,i} dS \) represents the scattered power through \( dS \). Within the Rayleigh-Debye approximation and assuming that absorption phenomena can be neglected, i.e. that the refractive index of the solid phase has zero imaginary part, the scattered light intensity can be straightforwardly calculated by means of the relationships presented in § 1.2.1. We should note, however, that in this case the incident light is incoherent. As a result the scattered light intensity has to be integrated over the incident light polarization angle. Taking the contribution to the scattered light intensity from the \( i \)-fold aggregate from Eq. (1.15) and expressing \( \hat{n}_i \cdot e \) as of Eq. (1.3) we write

\[
\frac{d\sigma_i}{d\Omega} = \frac{I_0^{2\pi} I_{f,d} d\phi R_d^2}{2\pi I_0} \frac{k_f^4}{16\pi^2} \frac{\delta e^2}{e_s^2} \frac{1 + \cos^2 \theta}{2} e_r^2 S_4(\theta) P(\theta),
\]  

where the structure factor and form factor were expressed in terms of the scattering angle, \( \theta \). Integrating over the solid angle we obtain the absolute scattering cross-section
for the \( i \)-fold aggregate

\[
\sigma_i = \int \frac{d\sigma_i}{d\Omega} = \frac{k_f^4 \delta \epsilon^2}{16\pi^2 \epsilon_s^2} i^2 \int_0^{2\pi} \int_0^{\pi} \sin \theta \partial \partial \theta \frac{1 + \cos^2 \theta}{2} S_i(\theta) P(\theta),
\]

(1.44)

which is further simplified to

\[
\sigma_i = A i^2 \int_0^{\pi} \sin \theta \partial \partial \theta \frac{1 + \cos^2 \theta}{2} S_i(\theta) P(\theta),
\]

where

\[
A \equiv \frac{k_f^4 \delta \epsilon^2}{8\pi \epsilon_s^2}
\]

is an optical constant. We note that the term \((1 + \cos^2 \theta)/2 < 1\) arises from the non coherency of the incident light.
2 Characterization of Colloidal Polymer Particles through Stability Ratio Measurements

2.1 Introduction

Aggregation phenomena in colloidal dispersions are of great importance in many industrial processes, such as in polymer, food and pharmaceutical industries or in water treatment. In the production and handling of polymer latexes, it is crucial to control the coagulation kinetics in order to achieve colloidal stability. The primary particle aggregation or doublet formation rate constant is one of the fundamental characteristics of a colloidal dispersion and it is relevant for the quantitative understanding of the kinetics of aggregation and stability of colloidal particles. The doublet formation rate constant is used to derive the so-called Fuchs' stability ratio, which provides a direct quantitative measure of colloidal stability. The doublet formation rate constant is also the starting point for the formulation of aggregation kernels that allow modeling the time evolution of the particle size distribution in aggregating dispersions using population balance equations [29]. Consequently the knowledge of the aggregation kinetics is a fundamental information for the efficient design and control of coagulation processes.

The stability ratio is controlled by interactions between primary particles due to dispersion, electrostatic, steric and other forces [30]. These interactions are strongly affected by the partitioning of various solutes, such as surfactants and salts, between the particle surface and the aqueous phase. It is therefore important to consider the adsorption and desorption behavior of water soluble components in the latex when studying the colloidal stability of latex particles. For example, when a given latex is diluted with pure water to different solid volume fractions, various species originally present at the polymer particle surface can partially transfer to the aqueous phase according to their adsorption equilibria, thus affecting the colloidal stability. This process is well recognized in the literature and extensive latex cleaning procedures are recommended to remove soluble components from the latex prior to aggregation kinetics measurements [31], in order to
obtain primary particles that are stabilized exclusively by species irreversibly attached to the polymer surface. Another possibility to obtain a system with the same surface chemistry at various latex dilutions is to separate a mother liquor from a stock latex and to use it as the diluting medium.

The primary particle aggregation rate constant can be measured by a variety of methods, such as turbidimetry [32–35], Coulter counter [36,37], static light scattering (nephelometry) [38–40], dynamic light scattering [41–43] and combined multiangle static and dynamic light scattering [44]. All these methods are based on measuring certain physical quantities as a function of time during aggregation, estimating the initial rate of change of these quantities at times where the process is dominated by primary particle aggregation, and finally deriving from this the doublet formation rate by means of relationships that depend upon the specific physical quantity measured. The problem is the evaluation of the initial rate of change of the measured quantity, which often reduces to the estimation of the initial slope in a plot of experimental data disturbed by experimental error. In addition, it is not easy to identify a priori the maximum time value that can be considered before doublet aggregation becomes significant. In this work we propose a procedure for estimating the doublet formation rate constant in aggregating colloidal dispersion of monodisperse spheres that overcomes these difficulties.

### 2.2 Estimation of Primary Particle Aggregation Rate

#### 2.2.1 Aggregation Kinetics

In colloidal dispersions particles collide due to Brownian motion and aggregate because of attractive dispersion forces. Aggregation kinetics can be modeled by the population balance equation (Smoluchowski coagulation equation), written for the $i$-fold aggregate as:

$$\frac{dN_i(t)}{dt} = \frac{1}{2} \sum_{l+m=i} K_{lm} N_l(t) N_m(t) - N_i(t) \sum_{j=1}^{\infty} K_{ij} N_j(t),$$

(2.1)

where $N_i$ is the number concentration of the $i$-fold aggregate, while $\{K_{lm}\}$ is the aggregation kernel which represents the matrix of second-order rate constants of aggregation between a $l$-fold aggregate and a $m$-fold aggregate and contains the entire information
about the physics of the aggregation mechanism. This means that the aggregation kinetics can be quantitatively described when an appropriate formulation for \( \{K_{in}\} \) is provided. Since the present work is mainly concerned with doublet formation rate we will focus our attention only on one element of \( \{K_{in}\} \), namely \( K_{11} \).

The simplest model of aggregation is obtained in absence of interparticle interactions where doublet formation is controlled by Brownian diffusion [7]:

\[
K_{11} = K_B = \frac{8kT}{3\mu},
\]

where \( k \) is the Boltzmann constant, \( T \) is the temperature and \( \mu \) the viscosity of the continuous phase.

In the more realistic situation where interparticle interactions are present, one obtains [30]

\[
K_{11} = \frac{K_B}{W},
\]

\[
W \equiv 2 \int_2^\infty \frac{\exp\left(\frac{U(\xi)}{kT}\right)}{G(\xi)\xi^{2}} d\xi, \quad \xi \equiv \frac{r}{R},
\]

where \( R \) is the particle radius, \( r \) is the interparticle distance, \( U(\xi) \) is the particle interaction potential, and the term \( G(\xi) \) accounts for the hydrodynamic resistance due to fluid outflow upon the mutual approach of two particles. \( W \) is the Fuchs' stability ratio, and its inverse is equal to the ratio between the primary particle aggregation rate and its value in the absence of interparticle interactions.

### 2.2.2 Early Stage Aggregation: Scaled Quantities

Here we consider the early stages of the aggregation process where we can assume that only primary particles and doublets are present. Under this assumption Eq. (2.1) leads to:

\[
N_1(t) = \frac{N}{1 + t/\tau_a}; \quad N_2(t) = \frac{N}{2} \frac{t/\tau_a}{1 + t/\tau_a},
\]

with \( N \equiv N_1(0) \) denoting the initial number concentration of primary particles and \( \tau_a \equiv (K_{11}N)^{-1} \) the characteristic time of aggregation. These relationships are asymptotically accurate at short times when the rate of doublet consumption is small compared to the
rate of its formation, i.e.
\[ \frac{K_{12}N_1(t)N_2(t)}{\frac{1}{2}K_{11}N_1(t)^2} \ll 1. \]

Using Eq. (2.5) and considering that \( K_{12} \) and \( K_{11} \) are of the same order of magnitude the relation above leads to
\[ \frac{2N_2(t)}{N_1(t)} = t/\tau_a \ll 1, \quad (2.6) \]
which provides a quantitative estimate of the time interval where Eq. (2.5) can be applied. Now, substituting Eqs. (2.5) in Eq. (1.40), we get
\[ R_{DLS}(t, q) = \frac{1 + 2S_2(q)t/\tau_a}{1/R + 2(S_2(q)t/\tau_a)/R_H^2}, \quad (2.7) \]
where the doublet structure factor is \( S_2(q) = \frac{1}{2}[1 + \sin(2Rq)/(2Rq)] \), which is obtained from Eq. (1.17) by setting \( i = 2 \) substituting \( g_2(r) = \delta(r - 2R)/(16\pi R^2) \), where \( \delta(\cdot) \) is the Dirac's delta function. The hydrodynamic radius of the doublet \( R_H^2 \) has been obtained from its diffusivity, which in the case of two touching solid primary particles gives \( R_H^2 \approx 1.38R \) [44].

Applying the same procedure to turbidity and scattered intensity, starting from Eqs. (1.42) and (1.15) respectively, we obtain
\[ \gamma^*(t) = \frac{\gamma(t)}{\gamma(0)} = 1 + \frac{g_2(t/\tau_a)}{1 + t/\tau_a}, \quad (2.8) \]
\[ \bar{I}^*(q, t) = \frac{I(q, t)}{I(q, 0)} = 1 + 2S_2(q)(t/\tau_a)/1 + t/\tau_a, \quad (2.9) \]
Once the radius of the primary particle \( R \) and the characteristic time of aggregation \( \tau_a \) are known, the time evolution of the measured hydrodynamic radius, non-dimensional turbidity and non-dimensional intensity can be predicted, within the time interval where condition (2.6) remains valid, using Eqs. (2.7), (2.8) and (2.9), respectively.

It is now convenient to rearrange Eqs. (2.7) to (2.9) in order to obtain linear relationships
2 Characterization of Colloidal Polymer Particles through Stability Ratio Measurements

in time:

\[
\varrho_{DLS}(t, q) \equiv \frac{1}{2S_2(q)} \frac{R_{DLS}(t, q)}{R - 1} = K_{11} N t,
\]

(2.10)

\[
\varrho_\zeta(t) \equiv \frac{\gamma^*(t) - 1}{2\sigma_1} = K_{11} N t,
\]

(2.11)

\[
\varrho_I(t, q) \equiv \frac{I^*(q, t) - 1}{2S_2(q) - I^*(q, t)} = K_{11} N t,
\]

(2.12)

where \( \alpha \equiv R/R^H_2 = 1/1.38 \), \( \sigma_2/2\sigma_1 \) can be obtained from Fig. 2.1 if the Rayleigh-Debye approximation condition [22] is met and \( \varrho_{DLS}(t, q) \), \( \varrho_\zeta(t) \) and \( \varrho_I(t, q) \) are defined as scaled hydrodynamic radius, turbidity and intensity, respectively, and can be computed from the corresponding quantity measured experimentally (i.e. hydrodynamic radius, turbidity or scattered light intensity) and the primary particle radius, \( R \). It is important to note that based on Eq. (2.6) the above equations strictly apply for

\[
0 \ll 1, \quad \varrho_\zeta(t) \ll 1, \quad \varrho_I(t, q) \ll 1.
\]

(2.13)

Thus, during an aggregation experiment we measure one of the relevant quantities men-
tioned above as a function of time, and we plot the corresponding scaled quantity versus time using Eqs. (2.12), (2.11) or (2.10). If in the initial region we obtain a straight line, then its slope is equal to $K_{11}N$. Note that such a straight line is certainly obtained in the region where condition (2.13) is satisfied. However, this can extend also to larger $\theta$ in the case where Eq. (2.6) is not valid, as for example if the doublets are less reactive than the primary particles.

### 2.2.3 Accuracy Assessment of The Estimation Procedure

The analysis above indicates that in order to minimize the systematic error in the estimate of $K_{11}$ due to the aggregation of doublets, the measurement time should be sufficiently short, i.e. $t \ll \tau_0$. On the other hand, we have to consider that every analytical technique has an instrumental random error, and therefore we need a sufficient duration of the experiment in order to be able to collect enough measurements to reduce the effect of such error on the obtained estimate of $K_{11}$. Let us look at the instrumental error in more detail. Let $\sigma_{\text{DLS}}$ be the standard deviation of the hydrodynamic radius measurement $R_{\text{DLS}}$; standard error analysis tells us that, starting from Eq. (2.10), the standard deviation $\sigma_{\theta}$ of the scaled hydrodynamic radius can be expressed as follows

$$\sigma_{\theta} = \frac{(1 - \alpha)\sqrt{1 + \left(\frac{R_{\text{DLS}}}{R}\right)^2}}{2S_2(q)R\left(1 - \alpha \frac{R_{\text{DLS}}}{R}\right)^2\sigma_{\text{DLS}}}.$$ 

If we collect $n_p$ measurements at times $t_j = j \tau_{\text{meas}}$, where $\tau_{\text{meas}}$ is the single measurement duration, then the slope $K$ estimated through linear interpolation (passing through the origin of coordinates, i.e. $\theta_{\text{DLS}} = 0$ at $t = 0$) of the scaled radii $\theta_{\text{DLS},j} = \theta_{\text{DLS}}(t_j, q)$ and the corresponding standard deviation $\sigma_K$ take this form

$$\tilde{K} = \frac{\sum \theta_{\text{DLS},j} t_j / \sigma_{\theta,j}^2}{\sum t_j^2 / \sigma_{\theta,j}^2},$$

$$\sigma_K = \frac{1}{\sqrt{\sum t_j^2 / \sigma_{\theta,j}^2}},$$

where $\sigma_{\theta,j}$ is given by the previous formula evaluated at $t_j$. As the number of measurements $n_p$ increases the standard deviation of the measured slope decreases until a certain number of experimental points $n_p^*$ is reached where the decrease is not noticeable anymore. Based on this observation alone one would want to decrease the measurement...
duration \( t_{\text{meas}} \) in order to increase the number of measurements in a given observation time. Yet, as for the standard deviation of the estimated slope, when a certain minimum value \( t_{\text{meas}}^* \) is reached the instrumental error of the single measurement \( \sigma_{\text{DLS}} \) will start to increase significantly. This means that the best measurement set-up yielding the minimum instrumental error in the shortest observation time is obtained when performing \( n_p^* \) measurements each of duration \( t_{\text{meas}}^* \).

However, as discussed above, the observation time has to satisfy the constraint (2.13), in order to avoid the significant formation of triplets. If this were not the case then a systematic error would be introduced, leading to an overestimation of \( K_{11} \) and thus an underestimation of the stability ratio. Consequently, for each experimental condition an optimal measurement setup exists that minimizes the sum of instrumental and systematic error.

This is illustrated in Figures 2.2 and 2.3 where the systematic and instrumental errors are shown together with their sum for a simulated typical example. In Fig. 2.2 the relative errors are plotted as a function of the number of measurements taken at constant measurement frequency (8.6 per unit \( \tau_a \)). In Fig. 2.3 the relative errors have been plotted as a function of the measurement frequency with constant number of measurements (equal to 4). The simulated experimental data on aggregation kinetics were generated by numerically solving Eq. (2.1) with the constant kernel [45]. The standard deviation for DLS measurements was assumed to be 2.6% of the hydrodynamic radius for the sake of illustration. However when considering a particular measurement the standard deviation should be estimated based on experimental data. The instrumental error was calculated by means of the formulas previously presented while the systematic error was computed as difference between the \( K_{11} \) value estimated through linear interpolation and the theoretical value used to simulate the experimental data. The calculated theoretical relative errors are independent of the actual values of \( K_{11} \) or \( N \).

It can be seen that as the experiment duration increases the systematic error increases, while the instrumental one decreases. This indicates that there are conditions where the total relative error is minimized and so the best estimate of \( K_{11} \) can be obtained, when we accept a certain systematic error introduced by the inaccuracy of the simplified kinetic scheme, while achieving a considerably lower instrumental error.

The above theoretical error analysis can also be applied for static light scattering and turbidimetry, using the corresponding functional forms of scaled quantities. However,
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Figure 2.2: Relative error in estimated value of the stability ratio for a simulated experiment as function of the number of measurements with constant frequency (8.6 measurement per unit $\tau_n$).

These techniques provide faster measurements with less fluctuations compared to DLS, so that smaller instrumental errors can be expected and shorter times can be used for measurements.

2.3 Experimental Section

2.3.1 Materials and Instruments

An emulsifier-free polymer latex was prepared by emulsion copolymerization of styrene (Fluka, purity $\geq 99\%$) and 2-hydroxyethyl methacrylate (HEMA) (Fluka, purity $\geq 99\%$) [46] following the polymerization recipe reported in Table 2.1. Potassium persulfate (KPS) (purity $\geq 99\%$) was used as initiator. The reaction was carried out in a 0.5 l jacketed reactor under nitrogen atmosphere at a stirring speed of 350 r.p.m. until 92.1% weight conversion was reached after about 20 hours. Table 2.2 summarizes the relevant properties of the final dispersion.
Figure 2.3: Relative error in estimated value of the stability ratio for a simulated experiment as function of the measurement frequency with total number of measurements equal to 4.

<table>
<thead>
<tr>
<th>Styrene</th>
<th>HEMA</th>
<th>KPS</th>
<th>Water</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.3 g</td>
<td>3.35 g</td>
<td>500 mg</td>
<td>450 g</td>
<td>75 °C</td>
</tr>
</tbody>
</table>

Table 2.1: Polymerization Recipe.

Solid content was measured by gravimetry (HG53 Halogen Moisture Analyzer, Mettler Toledo). Throughout all the experiments water was distilled twice and then filtered through a Millipore equipment. Sodium chloride (Fluka, Analytical Grade) was used to induce aggregation. DLS measurements were performed with an argon-ion laser M95-2 (Lexel) at 25 °C using a BI-200SM goniometer (Brookhaven) at the scattering angle of 50 °C.

2.3.2 The Aggregation Experiment

Aggregation in electrostatically stabilized colloidal dispersion is typically induced by the addition of an electrolyte, which screens the surface charges of the primary particles. Thus a typical aggregation experiment requires mixing of a colloidal dispersion with
<table>
<thead>
<tr>
<th>Solid Volume Fraction</th>
<th>DLS Diameter</th>
<th>Particle Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.0%</td>
<td>84 nm</td>
<td>$3.45 \times 10^{19}$ 1/m³</td>
</tr>
</tbody>
</table>

Table 2.2: Dispersion properties.

an electrolyte solution. This operation requires some comments since it may lead to significant experimental errors in aggregation kinetics measurements.

The aggregation process is in fact controlled by two characteristic times: the characteristic time of mixing $\tau_m$ and the characteristic time of aggregation $\tau_a$. In order to measure the true aggregation rate at the chosen electrolyte concentration we need to fulfill two requirements. First, the aggregation process should take place at uniform conditions in the entire vessel, which requires the mixing time to be much shorter than the aggregation time, i.e. $\tau_m \ll \tau_a$. Second, the aggregation itself should have a duration compatible with appropriate monitoring. However, in some conditions these two requirements may contradict each other.

When a volume $V_s$ of the electrolyte solution is mixed with a volume $V_d$ of the colloidal dispersion, local overshoots in both particle and electrolyte concentrations are experienced in the system before homogeneity is achieved ($t < \tau_m$). This might result in a significant extent of uncontrolled, and therefore undesired, aggregation. The concentration overshoots can be quantified by writing the following balances on particle and electrolyte concentrations, respectively

$$N = \frac{V_D}{V_D + V_S} N_D$$

$$I = \frac{1 - \phi_D}{1 - \phi} \frac{V_D}{V_D + V_S} I_D + \frac{1}{1 - \phi} \frac{V_S}{V_D + V_S} I_S,$$

here $N$ is the particle number concentration, $\phi = \frac{4}{3} \pi R^3 N$ is the solid volume fraction and $I \equiv \frac{1}{2} \sum z_i^2 c_i$ is the ionic strength in the final dispersion with $z_i$ and $c_i$ being the charge and the concentration of the $i$-th electrolyte, respectively. Subscripts $D$ and $S$ relate to the initial colloidal dispersion and salt solution, respectively, while no subscript refers to the final composition.

Let us first consider the case of ionic strengths above the critical coagulation concentration (CCC) in the diffusion limited regime, where the aggregation rate constant $K_{11}$ is independent on the electrolyte concentration. In such conditions $K_{11}$ is on the order of
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$10^{-17}$ m$^3$/s for aqueous solutions so that in order to conveniently monitor aggregation kinetics, we have to work at very low particle number concentrations $N$. For example, given a typical number concentration of a stock latex dispersion $N_D \approx 10^{21}$ m$^{-3}$, in order to achieve $\tau_a = (K_{11}N)^{-1} \approx 2$ hr, the dilution factor should be on the order of $10^{-8}$. Such dilution can be achieved either by taking the stock dispersion and diluting it with a salt solution to the target salt and particle concentration or by prediluting the original dispersion with water to a particle concentration $N_D$ very close to the desired $N$ and then adding a small volume of a concentrated salt solution. In the first case, the particle concentration overshoot occurs in the course of mixing and therefore it leads to undesired aggregation. In the second case, the salt overshoot takes place near the desired particle concentration but, since we are above the CCC, this overshoot in salt concentration does not affect the aggregation rate, thus allowing the experiment to take place at the desired conditions.

Now let us consider the case of aggregation experiment at ionic strength values substantially lower than the CCC, in this situation the salt concentration overshoot, proportional to $(I_S - I)$, must be minimized due to the extreme sensitivity of $K_{11}$ on this quantity [30]. On the other hand, since the value of $K_{11}$ is small, we need sufficiently large particle concentrations, $N$ in order to have a reasonable experiment duration. If we solve Eqs. (2.14) and (2.15) for $I_S - I$ we get

$$I_S - I = \frac{N}{N_D - N}(1 - \phi_D)(I - I_D), \quad (2.16)$$

which indicates that in order to minimize this difference one has to decrease $N$ and increase $N_D$. However, as seen above, there is a lower limit for the particle number concentration in the aggregating dispersion $N$ while an upper limit for $N_D$ is imposed by the particle concentration in the stock colloidal dispersion $N_D$. Thus the minimum attainable overshoot is:

$$I_S - I = \frac{N}{N_D - N}(1 - \tilde{\phi}_D)(I - \tilde{I}_D), \quad (2.17)$$

where $\tilde{\phi}_D$ and $\tilde{I}_D$ are the dispersion particle volume fraction and ionic strength in the stock colloidal dispersion, respectively and $N$ is the minimum value leading to a maximum tolerable aggregation timescale $\tau_a = 1/K_{11}N$. Note that this analysis implies that the lower is the target ionic strength, the smaller will be $K_{11}$, consequently the higher will be $N$ and the larger will be the ionic strength overshoot, thus indicating that for
any given colloidal system there exists a minimum salt concentration below which the doublet formation rate constant cannot be measured.

As discussed above, the relative amount of salt solution and latex as well as the corresponding concentrations and mixing procedure, have to be carefully selected for each aggregation experiment so as to minimize overshoots in salt and particle concentrations, and to obtain a reasonably short duration of the aggregation experiment where, however, the relevant part, i.e. \( t < \tau_0 \), should be sufficiently long to take proper measurements. In order to perform on-line DLS measurements substantial dilutions of the stock latex were required. To reduce the experimental error this was done in two dilution steps with water. Care was taken that the particle number concentration of the obtained dispersion was high enough to avoid salt overshoots in the last mixing step with the salt solution. Indeed in every experiments the salt concentration in the salt solution used to induce aggregation in the last step was always very near to the target salt concentration. Experiments were carried out in 20 ml glass beakers which were carefully washed and extensively rinsed with distilled water. Throughout sample preparation and its successive handling any dust contamination was carefully avoided.

### 2.4 Results and Discussion

Aggregation experiments were performed at three different dilution factors \( f \) while keeping the remaining experimental parameters fixed as detailed in Table 2.3. Each experiment consisted of four to six runs, so as to estimate mean values and standard deviations of the latex stability ratio \( W \) as a function of the latex dilution factor \( f \), and the corresponding polymer volume fraction, \( \phi \).

Figure 2.4 shows a typical measurement in terms of time evolution of the mean hydrodynamic radius for the run A1 corresponding to the experimental conditions A in Table 2.3.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>( I ) ([\text{mM}])</th>
<th>( \phi \cdot 10^7 )</th>
<th>( N \cdot 10^{-16} ) ([1/\text{m}^3])</th>
<th>( f \cdot 10^3 )</th>
<th>( W \cdot 10^3 )</th>
<th>std. dev. ( \cdot 10^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>225</td>
<td>8.56</td>
<td>3.45</td>
<td>1000</td>
<td>1.4</td>
<td>0.59</td>
</tr>
<tr>
<td>B</td>
<td>225</td>
<td>2.57</td>
<td>1.03</td>
<td>3333</td>
<td>0.58</td>
<td>0.21</td>
</tr>
<tr>
<td>C</td>
<td>225</td>
<td>0.856</td>
<td>0.345</td>
<td>10000</td>
<td>0.30</td>
<td>0.063</td>
</tr>
</tbody>
</table>

Table 2.3: Operating conditions in the aggregation experiments.
Once the evolution of the hydrodynamic radius over a period of time was measured, the corresponding values of the scaled radius $q_{DLS}$ were computed through Eq. (2.10) and plotted as a function of time, as shown in Figure 2.5 for the data of run A1 in Fig. 2.4. Shortly after $q_{DLS}(t, q)$ passes unity, which implies that time is of the order of $\tau_a$, a more-than-linear growth becomes evident. This is due to the occurrence of significant doublet aggregation that has been neglected in deriving Eq. (2.10). The scaled radius $q_{DLS}(t, q)$ in fact diverges for $R_{DLS}(t, q) = R_2^H$, condition that in the above simplified kinetic treatment is reached only at infinitely long times.

In Fig. 2.6 we show the evolution of the scaled radius at the early stages of aggregation where it exhibits a region of linear behavior in time. From the linear fit of the data in Fig. 2.6 according to $q_{DLS}(t, q) = K_{11} N t$ we estimate the doublet formation rate constant $K_{11}$ as the particle number concentration $N$ is known. Note that the linearity region extends to $q$ values which are relatively close to one. In our experience with polymer latexes we have observed that this is often the case, thus indicating that the condition $q \ll 1$ is too restrictive as discussed in the context of Eq. (2.13).

![Figure 2.4: Hydrodynamic radius as a function of time for run A1 corresponding to the experimental condition A in Table 2.3.](image)

The estimated values of $K_{11}$ together with the corresponding standard deviations are summarized in Table 2.3 in terms of stability ratios $W = K_B/K_{11}$. It is seen that the
stability ratio $W$ tends to decrease with increasing dilution factor $f$. However, this trend appears to be weak since the confidence intervals on $W$ are rather wide. Such scatter of the experimental data is not unusual for colloidal aggregation experiments and may be related to irreproducible desorption of small amounts of species from the polymer particle surface upon latex dilution, in addition to the well known sensitivity of the stability ratio to the solution ionic strength. On the other hand, the decreasing of colloidal stability with increasing latex dilution at a given ionic strength is not expected for nominally surfactant-free latexes as those considered in this work. Instead, in the presence of ionic surfactants this behavior would be justified by the desorption of surfactants upon dilution which leads to a decrease of the colloidal stability. This suggests that some surface active species might be nevertheless present in our latex owing to the peculiarities of the polymerization reaction.

In the first stage of styrene-HEMA emulsion copolymerization particles are homogeneously nucleated (i.e. with no surfactant) [46, 47]. Surface characterization studies [48, 49] showed the presence of both strong and weak acid groups on the polymer particle surface. Strong acid sites are due to the sulphonate groups originating from the initiator. Weak acid sites result from the oxidation [49 51] of HEMA alcoholic func-
2 Characterization of Colloidal Polymer Particles through Stability Ratio Measurements

Figure 2.6: Linear regression over the linear regime in Fig. 2.5.

...tion by persulphate, which is a strong oxidizing agent. Since the same process occurs also for the unreacted HEMA in solution we should expect the presence of weak acid groups also in the suspending medium. Since these molecules might effectively act as surfactants this could explain the observed effect of latex dilution on latex stability. In order to assess the magnitude of this effect we modeled the evolution of the emulsion copolymerization reaction with conversion (see Appendix for details). Results corresponding to our experimental conditions are shown in Figs. 2.7 and 2.8. Fig. 2.7 shows the weight conversion of each monomer ($Y_1$ for styrene and $Y_2$ for HEMA) as a function of the overall weight conversion. It is seen that HEMA is less reactive, that is, it adds more slowly to the polymer than styrene, resulting in a smaller final conversion at overall final conversion $X_f = 0.921$. The net result is that a fraction of HEMA greater than styrene is left unreacted and partitioned between polymer particle surface and the aqueous phase. Fig. 2.8 illustrates this phenomenon by showing the ratio $Z$ between the mass of HEMA dissolved in water and its total initial amount. The results show that at the final conversion, $X_f$ almost 8% of the initial HEMA is present unreacted in the latex.

Returning to the interpretation of the measured stability ratios, we have shown that there is a substantial amount of unreacted HEMA left in the latex at the end of the
2 Characterization of Colloidal Polymer Particles through Stability Ratio Measurements

polymerization. The unreacted HEMA has been likely oxidized to a weak acid which might act as a surfactant desorbing or adsorbing at the polymer particle surface upon changes in the latex solid volume fraction. This supports the proposed explanation that the observed decrease in colloidal stability with increasing dilution is due to the desorption of species, most likely the oxidized HEMA, which have a stabilizing effect on the polymer dispersion.

2.5 Conclusions

Aggregation kinetics of colloidal particles is commonly monitored by optical techniques such as dynamic light scattering, nephelometry or turbidimetry. In this work we have introduced a general procedure for the reliable estimation of the doublet formation rate constant or the corresponding stability ratio from measurements collected by any of the above techniques. In order to avoid the estimation of the initial slope of the plot of a measured quantity versus time, we propose a transformation of variables that leads to the definition of a scaled quantity which is expected to grow linearly in time, over a certain interval of time. The slope of the straight line interpolating the transformed
Figure 2.8: Ratio between the mass of HEMA dissolved in water and its total initial amount as a function of weight conversion.

We applied the proposed procedure to the measurement of the aggregation kinetics of primary particles in a styrene-HEMA latex prepared by surfactant-free emulsion copolymerization and diluted to various solid volume fractions. Although the latex is nominally surfactant-free, the stability ratio of the primary particles was found to decrease with latex dilution at a constant ionic strength. This was attributed to the presence of stabilizing species, most likely originating from the oxidation of non-reacted HEMA in the original latex.
2. Characterization of Colloidal Polymer Particles through Stability Ratio Measurements

2.A Sty-HEMA emulsion copolymerization modelling [1, 2]

At a given overall conversion value, $X$, the material balances on styrene (monomer 1) and HEMA (monomer 2) are as follows

$$M_1^0 - Y_1 X (M_1^0 + M_2^0) = M_1^m + V_p \phi_1 \rho_1,$$  
(2.18)

$$M_2^0 - Y_2 X (M_1^0 + M_2^0) = V_m \alpha_2 \rho_2 + V_w c_2^m + V_p \phi_2 \rho_2,$$  
(2.19)

where $c_2^m$ is the weight concentration of HEMA, $M_1^0$ and $M_2^0$ represent the initial amount in mass of monomer 1 and 2 respectively, $M_1^m$ the mass of styrene in the monomer phase, $V_m$, $V_p$ and $V_w$ the volumes of the monomer, particle and water phases, respectively, $\rho_i$ the density of monomer $i$, and $\alpha_i$ and $\phi_i$ the volume fraction of the $i$-th monomer in monomer and particle phase, respectively. Weight conversion and polymer weight compositions are defined as follows

$$X \equiv \frac{M_1^0 + M_2^0 - (M_1 + M_2)}{M_1^0 + M_2^0},$$

$$Y_1 \equiv \frac{M_1^0 - M_1}{M_1^0 + M_2^0 - (M_1 + M_2)},$$

$$Y_2 \equiv \frac{M_2^0 - M_2}{M_1^0 + M_2^0 - (M_1 + M_2)},$$

(2.20)

where $M_1$ and $M_2$ represent the mass of styrene and HEMA at a conversion $X$, respectively. Furthermore phase volumes can be expressed as follows

$$V_p = \frac{X (M_1^0 + M_2^0)}{\rho_p \phi_p},$$

$$V_w = \frac{M_2^0 \rho_w (1 - c_2^m)}{\rho_w},$$

$$V_m = \frac{M_1^m}{\rho_1 \alpha_1},$$

where $\phi_p$ is the volume fraction of polymer in the particles, $M_2^0$ the mass of water and $\rho_w$ its density, while the polymer density $\rho_p$ is expressed as follows

$$\rho_p = \frac{Y_1 MW_1 + Y_2 MW_2}{Y_1 V_1 + Y_2 V_2},$$
2 Characterization of Colloidal Polymer Particles through Stability Ratio Measurements

where \( \dot{V}_i \) are molar volumes and \( MW_i \) the molecular weights of the monomers.

Under the assumptions of (i) equirapartition between the two organic phases \([52]\), and

(ii) constant maximum swelling \([53]\) the following partitioning equations apply:

\[
\frac{\phi_1}{\phi_2} = \frac{\alpha_1}{\alpha_2},
\]

(2.21)

\[
\phi_p = 0.335,
\]

(2.22)

\[
c_2^w = \frac{\phi_2 \rho_2}{H_2},
\]

where \( H_2 \) is defined as the partitioning coefficient for HEMA between the monomer phase and water. It is important to note that the equations above are valid as long as the monomer phase is present, that is when \( M^{m}_1 \geq 0 \). In the absence of the monomer phase, the first terms in the right hand side of Eqns. (2.18) and (2.19) drop out and Eqns. (2.21) and (2.22) become not relevant.

Differentiation of \( Y_i \) as expressed in Eq. (2.20) with respect of \( X \) after some rearrangements yields the following expression

\[
\frac{dY_i}{dX} = \frac{Y_i}{X} - f_i
\]

where \( f_i = dM_i/d(M_1 + M_2) \) is obtained from the instantaneous monomer mass balances. In particular, introducing appropriate expressions for the kinetics of the relevant reactions and using the quasi steady state assumption, we obtain:

\[
f_i = \frac{\dot{V}_2 r_1 \phi_1^2 + \phi_1 \phi_2}{\dot{V}_1 r_1 \phi_1^2 + \frac{MW_1 + MW_2}{MW_1} \phi_2 \phi_2 + \frac{\dot{V}_2 MW_2}{\dot{V}_1 MW_1} \phi_2^2}\]

(2.23)

where \( r_i \) are the reactivity ratios.

Upon proper simplifications and rearrangements the final model equations are obtained as follows

\[
\frac{dY_i}{dX} = \frac{Y_i}{X} - \frac{\dot{V}_2 r_1 \phi_1^2 + \phi_1 \phi_2}{\dot{V}_1 r_1 \phi_1^2 + \frac{MW_1 + MW_2}{MW_1} \phi_2 \phi_2 + \frac{\dot{V}_2 MW_2}{\dot{V}_1 MW_1} \phi_2^2} \frac{1}{X} \]

(2.24)
with:

\[
\begin{align*}
M_1' &= M_1^0 - Y_1 X (M_1^0 + M_2^0) - V_p \phi_1 \rho_1, \\
M_2' &= M_2^0 - Y_2 X (M_1^0 + M_2^0) = V_m \alpha_2 \rho_2 + V_w c_{2}^{w} + V_p \phi_2 \rho_2, \\
V_p &= \frac{X(M_1^0 + M_2^0)(Y_1 \bar{V}_1 + Y_2 \bar{V}_2)}{(Y_1 M_W_1 + Y_2 M_W_2) \phi_p}, \\
V_w &= \frac{M_2^0}{\rho_w (1 - c_{2}^{w})}, \\
V_m &= \frac{M_1'}{\rho_1 (1 - \alpha_2)}, \\
\alpha_2 &= \frac{\phi_2}{\phi_p}, \\
\phi_1 &= 1 - \phi_p - \phi_2, \\
c_{2}^{w} &= \frac{\phi_2 \rho_2}{H_2}, \\
Y_2 &= 1 - Y_1,
\end{align*}
\]

for \(X \leq (M_1^0 - V_p \rho_1 \rho_1)/(Y_1 X (M_1^0 + M_2^0))\) and

\[
\begin{align*}
M_2' - Y_2 X (M_1^0 + M_2^0) &= V_w c_{2}^{w} M_W_2 + V_p \phi_2 \rho_2, \\
V_p &= \frac{X(M_1^0 + M_2^0)(Y_1 \bar{V}_1 + Y_2 \bar{V}_2)}{(Y_1 M_W_1 + Y_2 M_W_2) \phi_p}, \\
V_w &= \frac{M_2^0}{\rho_w (1 - c_{2}^{w})}, \\
\phi_1 &= 1 - \phi_p - \phi_2, \\
c_{2}^{w} &= \frac{\phi_2 \rho_2}{H_2}, \\
Y_2 &= 1 - Y_1,
\end{align*}
\]

for \(X \geq (M_1^0 - V_p \rho_1 \rho_1)/(Y_1 X (M_1^0 + M_2^0))\).

Eqns. (2.25) (or Eqns. (2.26) when applicable) provide \(\phi_1\) and \(\phi_2\) in terms of \(Y_1\), which in turn is used to integrate Eq. (2.24) backwards in conversion with initial condition \(Y_1 (X = 1) = M_1^0/(M_1^0 + M_2^0)\). The values of the parameters used in the simulations shown in Figs. 2.7 and 2.8 are reported in Table 2.4.

\[
\begin{array}{|l|c|c|c|}
\hline
\text{Parameter} & \text{Value} & \text{Units} & \text{Reference} \\
\hline
\bar{V}_1 & 115 & \text{ml/mol} & \text{\null} \\
\bar{V}_2 & 121 & \text{ml/mol} & \text{\null} \\
M_W_1 & 104.2 & \text{g/mol} & \text{\null} \\
M_W_2 & 130.1 & \text{g/mol} & \text{\null} \\
M_1^0 & 45.3 & \text{g} & \text{[54]} \\
M_2^0 & 3.35 & \text{g} & \text{\null} \\
M_2^0 & 270 & \text{g} & \text{\null} \\
H & 1.62 & \text{\null} & \text{\null} \\
\rho_1 & 0.906 & \text{g/ml} & \text{\null} \\
\rho_2 & 1.071 & \text{g/ml} & \text{\null} \\
\rho_w & 1 & \text{g/ml} & \text{\null} \\
r_1 & 0.53 & \text{\null} & \text{[55]} \\
r_2 & 0.59 & \text{\null} & \text{[55]} \\
\hline
\end{array}
\]

Table 2.4: Parameter values used in the simulation of the STY (1) HEMA (2) copolymerization.
3 Aggregation Kinetics of Polymer Nanoparticles Stabilized by Anionic Surfactant

3.1 Introduction

The preparation of polymer powders often starts with latices, i.e. aqueous suspensions of colloidal polymer particles stabilized by surfactants. The latex is destabilized in order to allow particles to aggregate and form particle clusters. In order to properly design such processes we need to rationalize how the latex stability depends on operating conditions, such as solid volume fraction, solution ionic strength and temperature.

In this chapter we study how the aggregation kinetics of primary particles in polymeric latices stabilized by an ionic surfactant is related to basic characteristics of the latex itself, such as particle size, volume fraction, solution concentrations of surfactant and salt. The surfactant adsorption results in formation of a diffuse electrical double layer around particles, from which interparticle repulsive forces arise providing colloidal stability. On the other hand, attractive interactions due to dispersion forces are driving the aggregation of particles. These two interactions are accounted for in the classical DLVO approach [11] which has been able to qualitatively and sometimes quantitatively explain various aspects of colloidal stability [56]. However, it has been noted that surface charging and its effect on colloidal stability often could not be consistently described when trying to reconcile results from various experimental characterizations. More specifically, it is known that the DLVO theory predicts a stronger dependence of the aggregation rate constant of primary particles on the solution ionic strength than that obtained in experiments [30]. In a recent careful study [57] two carboxylate polystyrene latices were comprehensively characterized using titration, electrophoretic mobility and aggregation kinetics measurements. An accurate description of surface charging in these latices was achieved with a Stern layer model of counterion binding based on titration data and for low surface charge ($\sigma < 5 \text{mC/m}^2$) conditions the DLVO based model of particle interaction energy resulted in quantitative agreement with aggregation kinetics measurements.
However, for higher surface charge densities a qualitative discrepancy between the measured and calculated aggregation rate constants for primary particles was observed. It was observed that in those cases where such discrepancies were obtained the maximum in the particle interaction energy was at surface-to-surface distances less than 1 nm. It was suggested that at these lengthscales the continuum assumptions used in deriving interaction energy expressions might be breaking down, so that the DLVO approach is no longer valid.

Here we would like to consider in what particular way the DLVO approach might be not valid for highly charged latices. We focus on the measurement of the rate of salt induced primary particle aggregation at different salt concentrations of a series of monodisperse polystyrene latices with varying particle size and surface charge (from adsorbed anionic surfactant) and use standard models for surface charging and colloidal stability to derive the corresponding charging behaviour. We then compare the so obtained charging behaviour to that previously obtained [3] for the same systems by means of electrophoretic mobility measurements. Limitations of the DLVO framework for highly charged latices such those considered here are thus illustrated.

3.2 Theoretical Framework

3.2.1 Surface charging

Electrostatic charge on the surface of primary particles stabilized by an anionic surfactant are due to negative dissociated groups (sulfate) of surfactant molecules (sodium dodecyl sulfate) adsorbed on the particle surface. The adsorption of surfactant molecules on the surface of latex particles results in the surface concentration of dissociable groups \( \gamma \) (mol/m\(^2\)). Assuming that all sulfate groups at the surface are dissociated, we obtain the bare surface charge density

\[
\sigma_0 = -F\gamma
\]  

(3.1)

where \( F \) is the Faraday constant. Since some sulfate groups at the surface might not be dissociated (as is the case in SDS micelles [58]), to calculate the net surface charge one has to consider the binding of the surfactant counterion (in this case, sodium) with the corresponding surface charge density \( \sigma_t \) (of the opposite sign than that of \( \sigma_0 \)).
Consequently, the net surface charge density $\sigma_1 + \sigma_0$ is determined by both the adsorption of the surfactant at the particle surface (quantified by $\gamma$) and the extent of its dissociation in the adsorbed state (quantified by the degree of counterion binding $\alpha = -\sigma_i/\sigma_0$).

An interplay between energy and entropy of dissociated counterions that are free to move in the aqueous phase, together with the requirement of macroscopic electrical neutrality, implies the presence of a diffuse part of the electrical double layer around each charged latex particle. The surface charge has to balance the diffuse layer charge per unit area of the charged surface $\sigma_d$, so that $\sigma_d + \sigma_1 + \sigma_0$, and thus the diffuse layer charge can be expressed using the surfactant coverage $\gamma$ and the degree of counterion binding $\alpha$

$$\sigma_d = F\gamma(1 - \alpha)$$  \hspace{1cm} (3.2)

The diffuse layer charge density $\sigma_d$ can be related to the electrostatic potential $\psi_d$ using an appropriate model describing the diffuse layer. In the case where only 1-1 electrolytes are present in the aqueous phase, the Gouy-Chapman model is physically reasonable and approximate analytical solutions to the (non-linear) Poisson-Boltzmann equation exist for the electrostatic potential in the diffuse layer around a spherical particle, for example:

$$\sigma_d = -\frac{\varepsilon k T \kappa}{e} \left[ 2 \sinh \left( \frac{e \psi_d}{2 k T} \right) + \frac{4}{\kappa a} \tanh \left( \frac{e \psi_d}{4 k T} \right) \right]$$  \hspace{1cm} (3.3)

This equation gives the surface charge density within 5% of an accurate numerical solution of the Poisson-Boltzmann equation for any value of the potential $\psi_d$ and $\kappa a > 0.5$ [30]. Here $a$ is the radius of the particle and $\kappa$ (the inverse of the Debye length) is given by:

$$\kappa = \sqrt{\frac{2 e^2 N_A I}{\varepsilon k T}}$$  \hspace{1cm} (3.4)

where the ionic strength $I$ is calculated as

$$I = \frac{1}{2} \sum_k c_k^\infty$$

where $c_k^\infty$ is the bulk concentration of ions of type $k$, $N_A$ is the Avogadro number, $e$ is the charge of an electron, $\varepsilon$ is the electric permittivity of the aqueous phase, equal to the product of vacuum permittivity $\varepsilon_0$ and the relative permittivity $\varepsilon_r$ (dielectric constant)
of water.

The inner part of the electrical double layer can be described by the Stern model, introducing two hypothetical planes parallel to the charged surface: the inner Helmholtz plane (IHP), where the bound counterions are located, and the outer Helmholtz plane (OHP), located outwards at some distance $\Delta_{\text{Stern}}$ (Stern layer thickness) from the IHP, where the diffuse layer starts. Thus the electrical potential is equal to $\phi_d$ at the OHP, while the electrical potential at the IHP is designated $\phi_i$. The Stern layer between the IHP and the OHP is ion free and acts as a condenser with the capacitance $C_s$, so that the inner layer potential can be related to the diffuse layer potential and charge as follows

$$\psi_d - \psi_i = \frac{\sigma_d}{C_s}$$  \hspace{1cm} (3.5)

It is usually not reliable to make a priori assumptions about the Stern layer capacitance and this is often used as a fitting parameter in trying to reconcile models with measured quantities. Under some conditions, however, the Stern layer capacitance can be deduced from titration experiments [59]. The binding of counterions $M_j^+$ to surface sites $S^-$ at the IHP is described by an equilibrium relation

$$K_j = \frac{[M_j S]_s}{[M_j^+]_{\text{iap}}[S^-]_s}$$

where $K_j$ is the counterion binding constant and $[S^-]_s$, $[M_j S]_s$ denote surface concentrations of the respective sites. $[M_j^+]_{\text{iap}}$ is the counterion concentration at the IHP, related to the bulk counterion concentration $c_j^\infty$ through the inner layer potential $\psi_i$ using the Boltzmann relation:

$$[M_j^+]_{\text{iap}} = c_j^\infty \exp\left(\frac{\psi_i}{kT}\right)$$

The overall degree of counterion binding $\alpha$ is then obtained from the surface charge balance [59]:

$$\alpha = \frac{\sum_j K_j c_j^\infty \exp\left(\frac{\psi_i}{kT}\right)}{1 + \sum_j K_j c_j^\infty \exp\left(\frac{\psi_i}{kT}\right)}$$  \hspace{1cm} (3.6)

The Stern layer capacitance $C_s$ determines the ability of the inner layer to adsorb ad-
Aggregation Kinetics of Polymer Nanoparticles Stabilized by Anionic Surfactant.

As the capacity decreases, more counterions can be bound in the inner layer electrostatically (due to increasing inner layer potential $\psi_i$). This is important when considering the charging of the surface with varying solution ionic strength.

When a colloidal particle surrounded by an electrical double layer is subjected to an external electrical field, it moves towards the electrode with the charge opposite to that of its surface. The corresponding velocity $v_F$ is such that the electrical force exerted by the electrical field is balanced by viscous friction [56]. An oscillating electrical field can be applied in order to force the particles to move back and forth within the measurement cell. The particle velocity is then measured with the help of laser Doppler velocimetry and the electrophoretic mobility is calculated as the particle velocity $v_F$ per unit of the applied electrical field $E$. The zeta potential $\psi_\zeta$ is then calculated from the measured values of the electrophoretic mobility using the model of O'Brien and White, considering double layer relaxation and retardation effects [60]. This model is accurate at moderate ionic strengths considered here, where conduction behind the shear plane is not expected to be significant [59]. In order to relate the zeta potential $\psi_\zeta$ to the diffuse layer potential $\psi_d$ we need to consider the distance of the shear plane from the particle surface $\Delta_{\text{shear}}$. Then the two potentials $\psi_\zeta$ and $\psi_d$ are related through

$$\tanh \left( \frac{e\psi_\zeta}{4kT} \right) = \tanh \left( \frac{e\psi_d}{4kT} \right) \exp \left( -\kappa\Delta_{\text{shear}} \right)$$

It is usually assumed that the shear plane distance $\Delta_{\text{shear}}$ is fixed for a certain range of conditions. However, an empirical relationship between the solution electrolyte concentration and the shear plane position has been found for colloidal particles [61] and surfactant micelles [62]. In both cases a linear relationship, $\Delta_{\text{shear}} = 0.2\kappa^{-1}$, between the shear plane distance and the Debye length (3.4) can be established.

3.2.2 Colloidal Interactions

There are two well recognized and amply documented kinds of interactions among colloidal particles in polymeric latices stabilized by ionic surfactants. First, there is an attractive dispersion force between two polymeric particles separated by another medium, arising due to electromagnetic fluctuations of the matter. This attractive interaction is the driving force for particle aggregation. In order to stabilize such a dispersion, ionic surfactants are often used to provide electrostatic stabilization. In this case, there is a
repulsive electrostatic force between two particles arising from the overlap between their diffuse electrical double layers in an electrolyte solution. An electrical double layer is present due to the surface charge of the ionic part of the adsorbed surfactant molecules, with a minor possible contribution from polymer chains with ionic endgroups generated by the initiator used during polymerization.

Here we assume in the spirit of DLVO that no other significant interactions are present and that the total energy of interaction between primary particles $U$ is expressed as the sum of the attractive dispersion contribution $U_{\text{dis}}$ and the repulsive electrical double layer contribution $U_{\text{edl}}$. In the case of spherical symmetry for the interaction force, the interaction energy $U$ varies in the radial direction only, so that it can be expressed as a function of dimensionless surface-to-surface distance between two particles $h = (r - 2a)/a$, where $a$ is the geometric radius of primary particles and $r$ is their center-to-center distance.

The attractive energy of interaction $U_{\text{dis}}$ can be explicitly calculated assuming that intermolecular dispersion forces are pairwise additive and integrating over the interior volume of two interacting particles. Hamaker [63] obtained the resulting expression for the dimensionless energy of interaction between two spherical particles:

$$U_{\text{dis}}(h) = -\frac{Ha}{6} \left[ \frac{2}{h(h+4)} + \frac{2}{(h+2)^2} + \ln \left( \frac{h(h+4)}{(h+2)^2} \right) \right]$$  \hspace{1cm} (3.8)

where $Ha$ is the dimensionless Hamaker constant. For polystyrene we use $Ha = 1.58$, corresponding the dimensional Hamaker constant $A = 6.510^{-21}$ J. We do not consider retardation effects [30] which are important over larger distances than those relevant to calculation of the stability ratio in our system, which are on the order of few nanometers.

The electrostatic repulsive interaction between two primary particles is caused by the overlap of their diffuse double layers. In order to calculate the energy of repulsion for the pair of particles, we need the diffuse layer electrostatic potential $\psi_d$, which is related to the diffuse layer charge density $\sigma_d$ through an appropriate model of the electrical double layer, as discussed in the previous section. In addition to physicochemical parameters discussed in the section on surface charging, the Stern layer thickness $\Delta_{\text{Stern}}$ determines the location of the outer Helmholtz plane, i.e. the distance from the surface where the diffuse layer starts, and so influences the interaction energy profile $U = U_{\text{dis}} + U_{\text{edl}}$. Larger thickness implies higher energy barrier and thus larger stability ratio $W$ for a given
diffuse layer potential \( \psi_d \). The Stern layer thickness is sometimes invoked to describe experimental data [64], while in other cases it is found to be not necessary [57].

When using the Stern model of the inner part of the electrical double layer, it was found that the double layer interaction energy is bracketed by two limiting regimes, where either the diffuse layer potential \( \psi_d \) or the surface charge density \(-\sigma_d\) remains constant [65]. If particles approach each other sufficiently slowly, electrostatic equilibrium can be maintained by redistribution of the surface charge, and hence the diffuse layer potential remains constant. In the other limiting case, during the time scale of a Brownian encounter, the diffusion of ions necessary to maintain electrostatic equilibrium might not be fast enough so that particles approach each other with constant surface charge rather than constant potential. Situations intermediate between these two limiting cases are described by the charge regulation regime taking into account shifting ionic equilibria during the particle approach [65]. Here we examine just the two limiting cases - constant potential (CP) and constant charge (CC) - in order to bracket the true surface charging behavior, whatever it might be.

In the literature there is a number of expressions available for the energy of repulsion of a pair of colloidal particles due to overlap of their electrical double layers (for an overview see [30,66]). Their ranges of applicability depend on the dimensionless thickness of the electrical double layer \((\kappa a)\) and the dimensionless diffuse layer potential \(\psi_d/kT\) of the particles. A linear theory suitable for small potentials \(|\psi_d/kT| < 1\) is based on the Debye-Hückel approximation (linearization of the Poisson-Boltzmann equation) to calculate exact repulsive interaction energy for two flat plates. Then one can use the Derjaguin approximation

\[
U_{\text{edl}}(h) = \pi a \int_0^{\infty} U_{\text{edl}}^{\text{plate}}(\eta) d\eta
\]

(3.9)

to calculate the corresponding interaction between spheres at separations small compared to their radius \((h \ll 1)\) by expanding the potential as a series in powers of \(1/\kappa a\) (so that it is required that \(\kappa a\) is large, cf. [30]). For the case of constant potential this approach was used by Hogg, Healy and Fürstenau [67] and for equal size spheres their expression simplifies to:

\[
U_{\text{edl}}(h) = \frac{2\pi \sigma a}{kT} \psi_d^2 \ln (1 + \exp (-\kappa ah))
\]

(3.10)
As potentials become larger, the linear theory becomes progressively less accurate compared to the full solution of the non-linear Poisson-Boltzmann equation. Oshima and Kondo [68] developed a more accurate approximation of the non-linear energy of interaction for the case of equal size spheres (again, it is required that $h \ll 1$ and $\kappa \gg 1$):

$$U_{\text{edl}}(h) = \frac{32\pi \varepsilon a}{kT} \left( \frac{kT}{e} \right)^2 \phi^2 \left\{ \left[ 1 + \frac{2\phi^2}{3} + \frac{23\phi^4}{45} \right] \ln \left[ 1 + \exp (-\kappa ah) \right] + \right.$$  

$$- \frac{\phi^2}{3} \left[ \left( 1 + \frac{22\phi^2}{15} \right) F_1 \left( \frac{\kappa ah}{2} \right) + \frac{1}{2} \left( 1 + \frac{23\phi^2}{30} \right) F_2 \left( \frac{\kappa ah}{2} \right) \right] +$$  

$$- \frac{\phi^4}{6} F_3 \left( \frac{\kappa ah}{2} \right) \right\} \quad (3.11)$$

where

$$\phi = \tanh \left( \frac{\psi_d}{4kT} \right)$$ \quad (3.12)

$$F_1(x) = x \left[ 1 - \tanh(x) - \frac{\tanh(x)}{2 \cosh^2(x)} \right]$$ \quad (3.13)

$$F_2(x) = \frac{1}{6 \cosh^2(x)}$$ \quad (3.14)

$$F_3(x) = \frac{1 - 11x \tanh(x)}{10 \cosh^4(x)} - \frac{x}{\cosh^6(x)}$$ \quad (3.15)

It can be seen that in the limit of $\psi_d \ll kT/e$ we recover the linear formula in Eq. (3.10).

For the case of constant surface charge a similar expression to that for a constant potential (3.10) was derived by Usui [69] and for equal size spheres it is:

$$U_{\text{edl}}(h) = -\frac{2\pi \varepsilon a}{kT} \psi_d^2 \ln \left( 1 - \exp (-\kappa ah) \right) \quad (3.16)$$

However, this expression becomes inaccurate for small separations, where the surface potential diverges to infinity as the surface charge is kept constant [70] and the Debye-Hückel approximation is no longer valid. While the constant potential expression (3.10) is accurate as the surface-to-surface gap $h$ diminishes to zero, the constant charge expression (3.16) is reliable only for $\kappa ah \gg \mid \psi_d e/kT \mid$ [71]. Therefore it is not suitable for the calculation of the stability ratio for aggregation kinetics.

However, one can use an analytical formula recently introduced by Oshima [71] based on approximates for the energy of interaction between two flat plates accurate at short
3 Aggregation Kinetics of Polymer Nanoparticles Stabilized by Anionic Surfactant

distances ($\kappa h < 2$):

$$U_{\text{dilute}}^{\text{plate}}(h) = 4\varepsilon \kappa \left( \frac{kT}{e} \right)^2 \ln \left[ \frac{1 + \exp \left( \sqrt{\cosh y(h)\kappa h} \right)}{1 + \exp \left( -\sqrt{\cosh y(h)\kappa h} \right)} \right] +$$

$$-\sqrt{\cosh y(h)} - 1 + 2 \cosh \left( \frac{y_0}{2} \right) + [y(h) - y_0] \sinh \left( \frac{y_0}{2} \right)$$

(3.17)

where

$$y(h) = \arcsinh \left( \frac{2 \sinh \left( \frac{y_0}{2} \right)}{\tanh \left( \frac{y_0}{2} \right)} \right), \quad y_0 = \frac{\varepsilon \psi_d}{kT}$$

(3.18)

and $\psi_d$ is the (undisturbed) diffuse layer potential at infinite separation. The energy of interaction between two equal spheres is then computed by numerical integration of the Derjaguin formula. For further details see [71].

3.3 Experimental

3.3.1 Preparation of Polystyrene Latex Dispersions

Latices were prepared by emulsion polymerization (see [4]). Styrene was chosen as monomer since in the literature on aggregation a polystyrene latex dispersion is often used as a model system. To avoid additional complexity, the only cations present were sodium ions from the emulsifier (sodium dodecyl sulfate, or SDS, C\textsubscript{12}H\textsubscript{25}SO\textsubscript{3}Na) and the initiator (sodium persulfate, Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8}), the same cations as from the salt (NaCl) used to destabilize the latex dispersions in aggregation experiments. A typical batch polymerization recipe was as follows: 10 g of sodium dodecyl sulfate (SDS) were dissolved in 937.5 g of distilled water and 200 g of styrene monomer was added. The emulsion was stripped by nitrogen to remove oxygen and further kept under nitrogen atmosphere. The batch was thermostated at 60°C and stirred at 400 rpm. Polymerization was initiated by adding 1 g of sodium persulfate. In the course of polymerization the monomer conversion was monitored by gravimetry. When the monomer conversion did not change further, hydroquinone inhibitor (in solid form) was added to eliminate any residual radical activity in the latex dispersion. Finally, the residual monomer was removed by stripping with nitrogen, with negligible accompanying loss of water. The mean hydrodynamic diameter

47
and polydispersity were determined by dynamic light scattering using the Zetasizer 5000 (Malvern Instruments). The final weight fraction of solids (polymer plus additives, i.e. initiator and surfactant) in the latex dispersion was determined by gravimetry, based on measuring the sample weight before and after complete drying. The drying process was carried out over a short time using the HG53 Halogen Moisture Analyzer (Mettler Toledo).

3.3.2 Aggregation Kinetics

The experimental procedure for aggregation kinetics measurements was as follows. First, 10 ml of a concentrated NaCl solution was added to 50 ml of the original latex dispersion (again diluting 1.2 times) so that the resulting mixture (after a short time of stirring to achieve aqueous phase homogeneity) reaches the desired NaCl concentration. Aggregation kinetics was followed through monitoring the time evolution of the mean hydrodynamic radius of the aggregating suspension. Particle concentrations in the dispersions were too high for on-line measurements of the scattered light intensity. Therefore, samples were withdrawn from the aggregating system and diluted with doubly distilled water to stop the aggregation. The measurements on these diluted samples were carried out with the Zetasizer 5000 (Malvern Instruments). The dynamic light scattering was performed at the scattering angle 90 degrees with the standard red light laser wavelength 632.8 nm.

3.3.3 Electrophoretic Mobility

Electrophoretic mobility of latices B and F was measured at different ionic strengths. Salt concentration was kept as low as to ensure latex stability during the measurements. The desired ionic strength was reached by dilution with NaCl solutions just as in the case of aggregation experiments, however, in order to keep surfactant coverage of latex particle under control, dilution factors were kept as low as 1.2. Further dilutions, imposed by the measuring technique, were achieved by dilution with mother liquor obtained by ultrafiltration of the respective sample. The measurements were carried out with the Zetasizer 5000 (Malvern Instruments).
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3.4 Results and Discussion

3.4.1 Characterization of Primary Particles

A standard one-step emulsion polymerization process has been adopted to produce latices with desired mean particle size by varying the amount of surfactant (emulsifier), while keeping the particle volume fraction approximately constant and the particle size distribution narrow. Table 3.1 summarizes reaction recipes (amount of styrene and SDS used) and properties of resulting latex dispersions (final mean particle diameter $d$ and solid weight fraction $w$). The weight fraction of solids is given by the mass ratio

\[
w_s = \frac{P + S + I}{P + S + I + W}
\]

where $P$, $S$, $I$, $W$ is mass of polymer, surfactant, initiator and water, respectively, assuming that only negligible amount of unreacted monomer is present in the latex after stripping. The mass ratio of polymer to water in the latex is then

\[
P \frac{1}{W} = \frac{w_s - \frac{S + I}{W} (1 - w_s)}{1 - w_s}
\]

<table>
<thead>
<tr>
<th>Latex</th>
<th>styrene [g]</th>
<th>SDS [g]</th>
<th>solid weight fraction</th>
<th>mean diameter [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>200</td>
<td>10</td>
<td>0.171</td>
<td>71</td>
</tr>
<tr>
<td>B</td>
<td>200</td>
<td>7.5</td>
<td>0.163</td>
<td>75</td>
</tr>
<tr>
<td>C</td>
<td>200</td>
<td>7.5</td>
<td>0.166</td>
<td>76</td>
</tr>
<tr>
<td>D</td>
<td>200</td>
<td>5.0</td>
<td>0.158</td>
<td>74</td>
</tr>
<tr>
<td>E</td>
<td>200</td>
<td>2.0</td>
<td>0.159</td>
<td>98</td>
</tr>
<tr>
<td>F</td>
<td>175</td>
<td>1.5</td>
<td>0.148</td>
<td>114</td>
</tr>
<tr>
<td>G</td>
<td>175</td>
<td>1.4</td>
<td>0.150</td>
<td>137</td>
</tr>
<tr>
<td>H</td>
<td>175</td>
<td>0.75</td>
<td>0.141</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 3.1: Properties of original (as prepared) latex dispersions: measured values. Amount of water: 937.5 g, amount of initiator: 1 g. * prepared by semi-batch reaction.
Neglecting volume contributions from surfactant and initiator we calculate the solid volume fraction 

\[ x = \frac{\rho_s}{\rho_s + \rho_w} \]

where \( \rho_s \) is polymer density and \( \rho_w \) is water density. Using the mean particle radius \( a \) and considering that the latices under examination are substantially monodisperse we obtain the particle concentration \( N \) (number of particles per unit volume of latex)

\[ N = \frac{x}{\frac{4}{3} \pi a^3} \]

and particle surface area per unit volume of latex

\[ S = 4N\pi a^2 \]

The values of each of these quantities, calculated for all experimental runs, are summarized in the first three columns of Table 3.2. The SDS in a latex is partitioned between the surface of the polymer particles and the aqueous phase. The overall mass balance for SDS in the latex dispersion is:

<table>
<thead>
<tr>
<th>Latex</th>
<th>( x )</th>
<th>( N \times 10^{14} ) [ml⁻¹]</th>
<th>( S ) [m²/ml]</th>
<th>( \gamma_0 )</th>
<th>% SDS adsorbed</th>
<th>( c_{s,aq} ) [mM]</th>
<th>( I ) [mM]</th>
<th>( S_2(q) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.156</td>
<td>8.34</td>
<td>13.2</td>
<td>2.32</td>
<td>98.3</td>
<td>0.768</td>
<td>14.2</td>
<td>0.866</td>
</tr>
<tr>
<td>B</td>
<td>0.150</td>
<td>6.806</td>
<td>12.0</td>
<td>1.93</td>
<td>98.4</td>
<td>0.537</td>
<td>14.0</td>
<td>0.851</td>
</tr>
<tr>
<td>C</td>
<td>0.153</td>
<td>6.67</td>
<td>12.1</td>
<td>1.90</td>
<td>97.9</td>
<td>0.526</td>
<td>14.0</td>
<td>0.848</td>
</tr>
<tr>
<td>D</td>
<td>0.147</td>
<td>6.94</td>
<td>11.9</td>
<td>1.30</td>
<td>98.5</td>
<td>0.290</td>
<td>13.7</td>
<td>0.855</td>
</tr>
<tr>
<td>E</td>
<td>0.150</td>
<td>3.05</td>
<td>9.21</td>
<td>0.671</td>
<td>98.2</td>
<td>0.124</td>
<td>13.6</td>
<td>0.764</td>
</tr>
<tr>
<td>F</td>
<td>0.140</td>
<td>1.81</td>
<td>7.37</td>
<td>0.634</td>
<td>98.0</td>
<td>0.116</td>
<td>13.6</td>
<td>0.699</td>
</tr>
<tr>
<td>G</td>
<td>0.142</td>
<td>1.06</td>
<td>6.22</td>
<td>0.696</td>
<td>97.5</td>
<td>0.130</td>
<td>13.6</td>
<td>0.607</td>
</tr>
<tr>
<td>H</td>
<td>0.134</td>
<td>2.41</td>
<td>7.87</td>
<td>0.300</td>
<td>98.4</td>
<td>0.0504</td>
<td>13.5</td>
<td>0.756</td>
</tr>
</tbody>
</table>

Table 3.2: Properties of original (as prepared) latex dispersions: calculated values. Polystyrene density \( \rho_p = 1.05 \) g/cm³, water density \( \rho_w = 1.00 \) g/cm³. Particle number concentration \( N \) and surface area \( S \) refer to the latex volume. SDS concentration \( c_{s,aq} \) and ionic strength \( I \) refer to the aqueous phase volume. \( \gamma_0 \) and \( c_{s,aq} \) : calculated using the SDS adsorption isotherm. Scattering vector modulus \( q = 1.87 \times 10^7 \) m⁻¹, \( \lambda_0 = 632.8 \) nm.
where \( c_{s,\text{tot}} \) is the total concentration of SDS in the latex dispersion, expressed in moles per liter of the aqueous phase. \( c_{s,aq} \) is the SDS concentration in the aqueous phase (in moles per liter of the aqueous phase). \( S_p \) is the particle surface in \( \text{m}^2 \) per liter of the aqueous phase, and \( \gamma \) is the surface coverage of SDS on the polymer particles in \( \text{mol/m}^2 \).

The surfactant adsorption isotherm \( \gamma = f(c_{s,aq}) \) is described well by a Langmuir-type adsorption isotherm [3]:

\[
\gamma = \frac{6.38 \cdot 10^{-3} c_{s,aq}}{1 + 1.45 \cdot 10^3 c_{s,aq}}
\]  

(3.20)

The SDS surface coverage \( \gamma_0 \), the aqueous phase concentration \( c_{s,aq} \) and the fraction of SDS adsorbed \( 1 - c_{s,aq}/c_{s,\text{tot}} \) for every original (as prepared) latex was calculated from Eqs. (3.19),(3.20) using the known amount of SDS used in the synthesis recipe. The obtained results are summarized in columns 5 to 7 in Table 3.2. It is seen that only about 2% of the total SDS amount remains in the aqueous phase. Note that for all latex dispersions studied here the surfactant concentration in the aqueous phase was well below the critical micelle concentration (cmc).

At the synthesis temperature used here only negligible amount of the initiator is consumed during the polymerization reaction and incorporated into polymer chains, so that essentially all the initiator is still present, in some form, in the latex aqueous phase. Bulk sodium concentrations in the aqueous phase of the original latex dispersions thus correspond to the sum of 8.96 mM from the total amount of the initiator (\( \text{Na}_2\text{S}_2\text{O}_8 \), possibly partially hydrolyzed to a sulfate) and a small contribution (0.1-0.8 mM, cf. column 7 in Table 3.2) from the surfactant, as verified by sodium analysis with Atomic Absorption Spectroscopy. The corresponding calculated ionic strength of the aqueous phase is close to 14 mM for all latices, as shown in column 8 of Table 3.2. This justifies the use of the same SDS adsorption isotherm (3.20) for all as synthesized latices considered here.

With the increasing ionic strength, as in the aggregation experiments, the surfactant adsorption is expected to increase. The saturation coverage at the cmc was reported to increase by about 30% when the NaCl concentration in the aqueous phase increased from 0 to 0.1 M, while at the same time the cmc of SDS decreased from 8.7 to 1.0 mM [72]. Since in all our experiments the ionic strength values between 40 and 330 mM (see
3 Aggregation Kinetics of Polymer Nanoparticles Stabilized by Anionic Surfactant

Tables 2 and 4) were used, we can bracket the surface coverage at any ionic strength considered here between the low calculated from the adsorption isotherm (3.20) for the original latex at the ionic strength 14 mM and the high calculated by assuming that 100% of the surfactant is adsorbed at polymer surface. The difference between the high and low bounds on the surfactant coverage is in all cases less than 2%.

3.4.2 Aggregation Kinetics

Following the methodology developed in Chapter 2, in the aggregation experiments we recorded the time evolution of the mean hydrodynamic radius \( R_{\text{DLS}} \) from DLS measurements (cf. Fig. 3.1). Table 3.3 lists conditions for all aggregation experiments, such as primary particle concentration \( N_0 \), aqueous phase ionic strength \( I \) and calculated surfactant surface coverage \( \gamma \). The two latex dispersions indicated with an asterisk (E* and F*) were prepared by adding 0.0425 g and 0.11 g of SDS to 50 ml of the original latex dispersions E and F, respectively. For each experiment we plotted the scaled mean hydrodynamic radius \( p_{\text{DLS}} \) as defined in Eq. (2.10) vs. time (cf. Fig. 3.1) and the slope of the initial linear part was obtained from linear regression. Dividing by \( N_0 \) we could estimate the primary particle aggregation rate constant \( K_{11} \).

For each experimental system we then solved the equation (cf. Eq. (2.3))

\[
\frac{4kT}{3\mu K_{11}a} = \int_0^\infty \frac{\exp \left( U_{\text{dia}}(r) + U_{\text{od}}(r) \right)}{G(r) r^2} dr
\]

for the unknown diffuse layer potential \( \psi_d \) in the electrostatic interaction energy expression \( U_{\text{cell}} \) given by Eqs. (3.11),(3.12) and (3.17), (3.18), (3.11),(3.9) for the constant potential and the constant surface charge limit, respectively. For the hydrodynamic function \( G(r) \) the following expression was adopted [73]

\[
G(h) = \frac{6h^2 + 4h}{6h^2 + 13h + 2} \quad h \equiv \frac{r - 2a}{a}
\]

Finally we calculated the corresponding diffuse layer charge \( \sigma_d \) from the Gouy-Chapman equation (3.3). Results for the constant potential case are shown in Table 3.3. In the case of constant charge the calculated diffuse layer potentials and the corresponding charges were 10-15% lower than those calculated for the constant potential case. Hereafter, for seek of clarity, we report only results based on the constant potential assumption since
Table 3.3: Aggregation experiments and surface charge calculations from DLVO adopting the constant potential assumption.
Figure 3.1: Mean hydrodynamic diameter versus time for several aggregation experiments performed with latex H.

no qualitative difference emerges from the adoption of the constant charge hypothesis.

In Fig. 3.2 we plot the apparent surface charge determined from aggregation experiments as a function of electrolyte concentration for all latices. It can be seen that there is a robust trend of the surface charge strongly increasing with electrolyte concentration. This is in disagreement with previous results [3] from electrophoretic mobility measurements performed on latices B and F (which are summarized in Table 3.4), indicating decreasing surface charge on sulfate groups due to counterion binding over a range of ionic strengths considered here.

Moreover, the obtained surface charge densities were substantially higher than those determined from electrophoretic mobility data and in one case (latex H3) even higher than the bare charge $\sigma_0$, i.e. $-\sigma_d > -\sigma_0 = F\gamma$, the maximum surface charge possible at the given surfactant coverage in the extreme of no counterions bound. Discrepancies between potentials from electrokinetic and aggregation measurements are commonly observed [66] and could in some cases be justified by considering that the position of the shear plane is shifted outward from the outer Helmholtz plane, thus registering lower values than the diffuse layer potential governing double layer repulsion between
Figure 3.2: Apparent surface charge vs. ionic strength from aggregation kinetics.

Table 3.4: Electrophoretic mobility measurements and zeta potential calculation for latices B and F at different ionic strengths [3].
3 Aggregation Kinetics of Polymer Nanoparticles Stabilized by Anionic Surfactant

particles [57]. In an attempt to use this approach to reconcile the surface charge densities obtained from aggregation kinetics through the DLVO theory with those obtained from electrophoretic mobility measurements, we found that \( \Delta_{\text{shear}} = 0.35 \text{ nm} \) and \( 0.75 \text{ nm} \) was needed for latices B and F, respectively. Although the lower value for latex B might be reasonable, it is not clear why the shear plane of latex F would be located so far, more than twice as far as for latex B (for comparison, primary particles are 50\% larger and surfactant coverage is 3 times lower for latex F than for latex B).

This discrepancy is demonstrated for latices B and F in Figs. 3.3(a) and 3.3(b), respectively, where we show surface charge densities determined from electrophoretic mobility measurements (calculated from \( \psi_c \) in Table 3.4 using Eqs. (3.3) and (3.7) with \( \Delta_{\text{shear}} \) as indicated) and those from the aggregation kinetics through the DLVO theory as explained above in this section. Although one could formally resolve this disagreement between surface charges by setting an appropriate value of the shear plane position \( \Delta_{\text{shear}} \), as shown, it is not clear why the shear plane should be so far away and at a different position for each latex at rather high ionic strengths (\( >150 \text{ mM} \)) used here. However, even more importantly than the discrepancy in the charge magnitude, we still cannot account for the fact that the apparent surface charge determined from aggregation experiments increases significantly with increasing electrolyte concentrations.

3.4.3 Additional Repulsion Beyond DLVO

In the section above we have found that the surface charge that one estimates using DLVO theory in order to reproduce the observed aggregation kinetics is sometimes unaccountably larger than that estimated from electrophoretic mobility. Even more significantly, the apparent surface charge determined from aggregation kinetics increases strongly with increasing electrolyte concentration, contrary to the decreasing surface charge estimated from electrophoretic mobility. Since the latter is a more direct, and therefore reliable estimate, we can attribute this discrepancy to the DLVO theory, which would then tend to underestimate the interparticle repulsion energy.

In order to correct the surface charge values estimated from aggregation kinetics (cf. Fig. 3.2) we postulate an additional repulsive term with a simple exponential decay in the expression for the particle interaction energy. For two flat plates the repulsive energy...
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Figure 3.3: Surface charge versus ionic strength. (a) latex B: lines represents the values calculated from $\psi_e$ in Table 3.4 using Eqs. (3.3) and (3.7) with $\Delta_{\text{shear}} = 0.2 \text{ nm}$ (dashed line) and $\Delta_{\text{shear}} = 0.35 \text{ nm}$. filled circles and filled squares represent the values obtained from the aggregation experiments through the DLVO model and the modified DLVO model (see § 3.4.3), respectively. (b) Latex F: lines represents the values calculated from $\psi_e$ in Table 3.4 using Eqs. (3.3) and (3.7) with $\Delta_{\text{shear}} = 0.2 \text{ nm}$ (dashed line) and $\Delta_{\text{shear}} = 0.75 \text{ nm}$, filled circles and filled squares represent the values obtained from the aggregation experiments through the DLVO model and the modified DLVO model (see § 3.4.3), respectively.
expression with an exponential decay can be generally written as:

\[ U^{\text{plate}}(d) = A_{\text{rep}} \exp\left(-d/\lambda_{\text{rep}}\right) \]

where \( A_{\text{rep}} \) is a repulsive energy (scaled by \( kT \)) per unit area, \( d \) is the surface-to-surface distance and \( \lambda_{\text{rep}} \) is a corresponding decay length. Of course, both \( A_{\text{rep}} \) and \( \lambda_{\text{rep}} \) can in principle depend on physicochemical properties of the particle surface and the solution composition. The corresponding expression for the repulsive energy between two spherical particles with radius \( a \) is then calculated using the Derjaguin approximation (3.9):

\[ U_{\text{rep}}(h) = \pi a \lambda_{\text{rep}} A_{\text{rep}} \exp\left(-a h/\lambda_{\text{rep}}\right) \] (3.22)

It has been proposed by Israelachvili and others ([74] and references therein) that additional repulsive interactions upon the close approach of two surfaces can arise from dehydraion of small positively charged counterions. Another possible source of additional repulsion are interactions between ion-pair dipoles at partially charged surfaces where counterion binding is significant [75]. The concept of the hydration force was born out from direct force measurements, but is also experimentally supported by an earlier work on colloidal stability [70], where the observed stability behavior was in line with the DLVO theory when using larger cations with less hydration tendency, such as Cs\(^+\), while with the more hydrated Na\(^+\) the stability region extended to high ionic strength values well beyond the expected critical coagulation concentration. The additional repulsive interaction in the surfactant stabilized system could thus be attributed to a variety of possible sources: dipole-dipole interactions, dehydration of sodium surfactant counterions or steric repulsion between surfactant molecules upon the close approach of two aggregating particles.

The total particle interaction energy accounting for the additional repulsive interactions is now defined as the sum of the dispersion, electrical double layer and repulsion contributions:

\[ U(h) = U_{\text{dis}}(h) + U_{\text{edl}}(h) + U_{\text{rep}}(h) \] (3.23)

For a given primary particle radius \( a \), surfactant coverage \( \gamma \) and solution ionic strength \( I \) we can now in principle calculate the diffuse layer potential and charge from Eqs. (3.2), (3.3), (3.5), (3.6), and then the corresponding stability ratio \( W \) from Eq. (2.4) with the
interaction energy given in Eq. (3.23). On the other hand, we can take a value of $W$ known from an aggregation experiment and solve the same system of equations for the unknown parameters of the repulsion energy term (3.22).

In order to obtain an estimate of $A_{\text{rep}}$, we chose the decay length equal to about two solvent diameters, $\lambda_{\text{rep}} = 1$ nm, of the order of magnitude for short range repulsive interactions estimated from direct force measurements [74]. Then we estimated the repulsive parameter $A_{\text{rep}}$ for each aggregation experiment for latices B and F from Table 3.3. In the computation the counterion binding expression given in Eq. (3.6) was rewritten for the electrolyte at hand as

$$\alpha = \frac{K_{\text{Na}}I \exp(\psi_d/kT)}{1 + K_{\text{Na}}I \exp(\psi_d/kT)}$$

(3.24)

were we adopted an infinite Stern layer capacitance [3]. Using the the counterion binding constant $K_{\text{Na}} = 6$ dm$^3$/mol [3] we obtained $A_{\text{rep}} = 0.75$ (±0.25) mJ/m$^2$ for all latices. The magnitude of $A_{\text{rep}}$ estimated here is about one order of magnitude smaller than typical values determined from direct force measurements between mica surfaces in monovalent salt solutions [56]. In Figs. 3.3(a) and 3.3(b) we show that the calculated surface charge is now in a reasonable agreement with values estimated from electrophoretic mobility measurements adopting a shear plane distance, $\Delta_{\text{shear}}$ of 0.2 nm.

We note that the additional repulsive term in the interaction energy (3.23) results in the calculated stability ratio depending less sensitively on the ionic strength than the classical DLVO theory predicts. This is seen in Figs. 3.4(a) and 3.4(b), where we plot the calculated dependence of the stability ratio on solution ionic strength using DLVO interactions with and without the additional repulsive term (3.22). This effect might be related to the often noticed discrepancy that for highly charged latices the measured stability ratio depends less strongly on the solution ionic strength than the DLVO theory suggests [76]. The actual slope of the logarithm of the stability ratio vs. ionic strength is determined by an interplay of numerical values of interaction parameters, $H_a$, $A_{\text{rep}}$, $\lambda_{\text{rep}}$, which in principle depend on both the surface charge density and solution ionic strength, although the actual functional dependencies for these quantities are not known. In addition, it has been recently pointed out that electrical double layer repulsion and dispersion attraction are not independent and should be treated in a coupled fashion for quantitative description of interparticle interactions at high ionic strengths [77]. Since at the moment no direct evidence is available to relate the repulsive interaction energy
Figure 3.4: Stability ratio versus ionic strength. (a) Latex B: filled circles represent the experimental points in Table 3.3, long dashed and dashed lines represent the values calculated from standard DLVO model with $\Delta_{\text{shear}} = 0.2$ nm and $\Delta_{\text{shear}} = 0.35$ nm, respectively, solid line represents the points calculated from the DLVO model with the additional repulsion term in Eq. (3.22) with $A_{\text{rep}} = 0.75 \pm 0.25 \text{ mJ/m}^2$ obtained from independent electrophoretic mobility measurement. (b) Latex F: filled circles represent the experimental points in Table 3.3, long dashed and dashed lines represent the values calculated from standard DLVO model with $\Delta_{\text{shear}} = 0.2$ nm and $\Delta_{\text{shear}} = 0.35$ nm, respectively, solid line represents the points calculated from the DLVO model with the additional repulsion term in Eq. (3.22) with $A_{\text{rep}} = 0.75 \pm 0.25 \text{ mJ/m}^2$ obtained from independent electrophoretic mobility measurement.

parameters to the system properties or indeed to obtain a quantitative treatment of an interplay between electric double layer and dispersion interactions, the above approach should be considered as an empirical correction to the DLVO theory capable of explaining our experimental data on aggregation kinetics of highly charged polystyrene latices.

3.5 Conclusions

Aggregation rate constants of primary particles were measured for various combinations of particle size, surfactant coverage and electrolyte (NaCl) concentration such that particles were aggregating slowly (with Fuchs stability ratios of the order of $10^5$ to $10^9$). From the measured stability ratios we calculated diffuse layer potentials using the particle in-
interaction energy accounting for the dispersion attraction and the diffuse double layer repulsion in a DLVO framework. Diffuse layer potentials and the corresponding surface charge densities were calculated for both constant potential and constant charge limiting regimes, using appropriate expressions based on the non-linear Poisson-Boltzmann equation. The apparent surface charge densities calculated in this way were substantially higher than those determined from electrophoretic mobility data and in one case even higher than the maximum possible value at the given surfactant coverage in the extreme of no counterions bound. Moreover, the apparent surface charge increased significantly with increasing electrolyte concentration for all latices, contrary to the results from electrophoretic mobility measurements indicating a decreasing surface charge for a given latex due to counterion binding. The observed discrepancies indicate that these highly charged latex particles in sodium chloride solutions repel each other stronger than expected from the classical diffuse double layer DLVO theory. The additional repulsion can be qualitatively described by postulation of a repulsive term with a simple exponential decay in addition to the DLVO particle interaction energy. The additional repulsive interaction could be related to dipole-dipole interactions, dehydration of sodium surfactant counterions or steric repulsion between surfactant molecules upon the close approach of two aggregating particles. However, since at the moment no direct evidence is available to relate the repulsive interaction energy parameters to system properties or indeed to obtain a quantitative treatment of an interplay between electric double layer and dispersion interactions in high salt systems, the extended DLVO approach should be considered as an empirical correction capable of explaining our experimental data on aggregation kinetics of highly charged polystyrene latices.
4 Modeling the Focused Beam Reflectance Measurement

4.1 Introduction

Knowledge of the particle size distribution (PSD) is a vital piece of information in processing wet and dry powders in the micrometer to millimeter size range. Several techniques are available to obtain such an information (c.f. [78] and [79]), each of which has its own peculiarities. However, when considering on-line in-situ measurements in the volume fractions ranges typical of industrial processes the choice becomes much more limited. On the other hand, on-line in-situ measurements are of paramount importance not only for process control purposes but also in the in process research and development, where one would ideally like to assess the relevance and effect of any process parameter without the need of sampling. Focused beam reflectance method (FBRM) [80, 81] (also called laser backscattering) is a technique that provides robust in-situ measurements up to volume fraction as high as 40%. Owing to its measuring principle, however, the measured quantity is not directly the PSD but the so called chord length distribution (CLD). The CLD is the result of a convolution between the PSD and the particular shape of the particles under examination, represented by the single particle CLD multiplied by an appropriate weight function.

Concerning the modeling details of the convolution no consensus has yet been established in the literature. The CLD for a monodisperse population of spheres, i.e. the single particle CLD, is available together with a numerical procedure for computing the single particle CLD of particles of any convex shape [82]. In the more complex case of polydisperse populations the relation between PSD and CLD is much less understood. For spherical particles, different weights for the PSD convolution have been proposed [83-85]. Recently Wynn [86] provided a detailed mechanistic modelling of spherical particle detection and proved that this weight should actually be the particle radius, as previously proposed by [87]. He then heuristically extended these results to
4 Modeling the Focused Beam Reflectance Measurement

the case of non spherical particles by proposing to use a characteristic particle size which is however not defined.

In this work we develop a detailed mechanistic model for the detection of particles of any convex shape. Based on this result we derive the explicit definition of the shape-dependent characteristic length appearing as a weight in the convolution relationship between PSD and CLD. Then we rigorously derive relationships between the PSD and the CLD moments for particles of any convex shape. In the second part of the paper we illustrate how the modeling results can be properly used for sizing particles of unknown shape. It is clear that these results are fundamental for making the FBRM technique able to provide quantitative information about the particle size distribution.

4.2 Measurement Principle

A FBRM device is constituted by a tubular probe which is inserted into the flowing medium to be analyzed. At the probe tip a laser beam is shined, parallel to the axis of the probe, into the medium through a sapphire window and highly focused right beyond it. The beam itself is rotated around the axis of the probe at high speeds (2m/sec to 6m/sec, depending on the application) so that, as a particle with a sufficiently high refractive index passes near its focal point, the laser beam is backscattered while tracing a path on the particle itself, thus performing a "cut" on it. The backscattered light intensity is then converted into an electronic signal to be analyzed by a discrimination circuit. The logic of the circuitry recognizes the peaks corresponding to particle cuts and calculates their durations. Knowing the rotational speed of the laser beam, the durations can be easily converted into the corresponding path lengths that the laser beam has traveled through the detected particles. During each predetermined measuring time interval the detected cuts are sorted out in a predefined size grid, so that the final measurement result is the number of cuts that, in the measuring interval, fall within each bin of the grid.
4.3 Particle Detection Modeling

In order to derive the CLD for a collection of particles, the contribution of each one must be properly taken into account. Let us first consider the simplest case where the following assumptions are satisfied:

1. the laser beam diameter is much smaller than the size of the particles,

2. there is only one extinction length $c$ for all the particles,

3. the particle number concentration near the sapphire window is equal to that in the bulk (no influence of the boundary layer),

4. the particle residence time in the detection volume is much smaller than the laser emitter revolution time,

5. monodisperse population of spherical particles of radius $l$.

The function $f(c, l)$, where $c$ is the cut length (or chord length), is defined so that

\[ f(c, l)dc \partial l = X_p(c, l)dc \times R_d(l)dl, \tag{4.1} \]

where evidently, owing to its definition, $X_p(c, l)$ is the single particle CLD. Fig. 4.1A and 4.1B represent schematically the upper and lateral view, respectively, of the moving laser (dash-dotted line), together with several possible placements of particles of size $l$ are shown. If $v$ is the linear velocity of the laser beam then in an interval of time $\Delta t$ it will travel a distance $v \Delta t$. During this period of time gray particles will not be detected either because they lie outside of the focus zone (i.e. farther than the extinction length $c$ from the focal plane) and their backscatter is too weak to be detected (cartoon B), or because they are not hit by the laser beam at all (cartoon A) since their center is farther than a distance $l$ from the laser axis. We can then deduce that only those particles whose center is contained in the parallelepiped of size $c \times 2l \times (v \Delta t)$ are detected, consequently
we can write

\[ R_d(l) \Delta t = \frac{2e2\nu \Delta t N_p \Lambda(l) \Delta l}{\Delta t} = e2\nu N_p \Lambda(l) \Delta l, \]

where \( N_p \) is the particle number concentration and \( \Lambda(l) \) the PSD normalized to one. Substituting Eq. (4.2) into Eq. (4.1) we get

\[ f(c, l) \Delta c \Delta l = X_p(l, c) \Delta c \times 2e2\nu N_p \Lambda(l) \Delta l, \]

which expresses the concept that the probability for each particle to be cut is proportional to its size, thus implying that its contribution must be weighted by its characteristic length.

When a particle of any shape is considered, matters get considerably more complicated. We consider now the same assumption as above, but we replace the fifth one with the less stringent assumption that the particles can be of any convex shape, but such that their geometry can be described by a single parameter, \( l \). Under these assumptions the projection of a particle on the plane orthogonal to the laser beam will in general depend
on its orientation in space as opposed to the case of a spherical particle. In order to count the number of detections of a particle of a given size times the probability that this detection corresponds to a cut of length \(c\) let us consider a particle of any convex shape as shown in Fig. 4.2. If \(s(u,v)\) is the parameterized surface of the particle where \(s\) is the vector connecting the center of mass to the point on the surface, we can identify every possible limiting position of a particle being detected with the unit vector \(\hat{s}\) corresponding to the point of the surface of the particle tangent to the plane swept by the laser and the angle \(\theta\) which specifies the rotation of the particle around the axis orthogonal to the laser plane. Within this description Eq. (4.3) can be rewritten for the configuration \((\hat{s}, \theta)\) as follows

\[
f(c, l, \hat{s}, \theta) \partial c \partial l \partial n \partial\theta/(2\pi) = X_p(l, c, \hat{s}, \theta) 2 e 2l' v N_p A(l) \partial l \partial c \partial n \partial\theta/(2\pi), \tag{4.4}
\]

here \(l'\) is the distance of the center of mass from the laser plane, \(\partial n\) is the differential fraction of particles tangent to the laser plane, \(\partial\theta/(2\pi)\) is the differential fraction of particles rotated of an angle \(\theta\) around the normal to the laser plane. The term \(X_p(l, c, \hat{s}, \theta)\) deserves a special note. Indeed in Eq. (4.4) the factor 2 arises from the fact that we are counting the cuts corresponding to the configurations represented in Fig. 4.2 as the dashed contour (i.e. those for which the center of mass lies above the laser plane) and then multiplying by 2 in order to include those corresponding to the configurations where the center of mass lies below the laser plane shown in Fig. 4.2 as a dash-dotted contour. This consideration implies that the term \(X_p(l, c, \hat{s}, \theta)\) is defined as the probability density that the length of the cut of the laser plane on the contour of the projection onto the plane orthogonal to the laser plane of a particle whose characteristic size is \(l\) and whose
configuration is \((\hat{\text{s}}, \theta)\) is c, given that the laser plane is comprised between the center of mass and the point s.
Since the only term depending on \(\theta\) is \(X_p(l, c, \hat{\text{s}}, \theta)\) this variable can be integrated out thus obtaining
\[
f(c, l, \hat{\text{s}}) \partial c \partial l \partial n = \tilde{X}_p(l, c, \hat{\text{s}}) 2e 2l' v N_p \Lambda(l) \partial l \partial c \partial n,
\]
where \(\tilde{X}_p(l, c, \hat{\text{s}}) = \left( \int_0^{2\pi} X_p(l, c, \hat{\text{s}}, \theta) d\theta \right) / 2\pi\).
To account for all possible tangent points Eq. (4.5) must be integrated over \(dn\) thus yielding
\[
f(c, l) \partial c \partial l = \left( \int \tilde{X}_p(l, c, \hat{\text{s}}) l' dn \right) 2e 2v N_p \Lambda(l) \partial l \partial c.
\]
If we define the single particle chord length distribution as
\[
X_p(l, c) = \frac{\int \tilde{X}_p(l, c, \hat{\text{s}}) l' dn}{\int l' dn},
\]
and the characteristic length as\(^1\)
\[
l = \int l' dn,
\]
we obtain once again Eq. (4.3). The last two definitions mark two very important results. By providing an accurate model for non-spherical particle detection we have been able to give a rigorous expression for the single particle chord length distribution and, more importantly, we have shown that the characteristic length describing the size of a particle cannot arbitrarily be chosen, but is a specific function of particle shape. In particular, this is given by the average of the distances of the center of mass from all the planes tangent to its surface, which in case of a sphere obviously corresponds to its radius, which is in agreement with earlier treatments on spheres \([86, 87]\). We can rewrite Eq. (4.8) in a more explicit form as follows. If \(T_u = \partial s / \partial u\) and \(T_v = \partial s / \partial v\) are the tangent vectors of the parameterized surface \(s(u, v)\) then \(dn\) and \(l'\) can be expressed as

\(^1\)It can be easily demonstrated that this quantity does not depend on the arbitrary choice of identifying particle’s positions with their centers of mass.
follows
\[ dn = \frac{dS}{S}, \]
\[ l' = \frac{|s(u, v) \cdot (\mathbf{T}_u \times \mathbf{T}_v)|}{|\mathbf{T}_u \times \mathbf{T}_v|}, \]
where \( S = \int_{s} |\mathbf{T}_u \times \mathbf{T}_v| \partial u \partial v \) is the measure of the surface of the particle while for \( l' \) we exploited the feature that it is the projection of \( s \) along the normal to the tangent plane \( |\mathbf{T}_u \times \mathbf{T}_v| \). It follows that
\[
\int l'dn = \int \frac{|s(u, v) \cdot (\mathbf{T}_u \times \mathbf{T}_v)|}{|\mathbf{T}_u \times \mathbf{T}_v|} \frac{dS}{S} \]
\[
= \int \frac{|s(u, v) \cdot (\mathbf{T}_u \times \mathbf{T}_v)|}{|\mathbf{T}_u \times \mathbf{T}_v|} \frac{|\mathbf{T}_u \times \mathbf{T}_v| \partial u \partial v}{S} \]
\[
= S^{-1} \int s(u, v) \cdot (\mathbf{T}_u \times \mathbf{T}_v) \partial u \partial v. \] (4.9)

Upon integration of Eq. (4.3) over \( l \) we obtain the total CLD, \( X(c) = \int_{0}^{\infty} f(c, l) dl \) from the PSD
\[ X(c)dc = \left( \int_{0}^{\infty} 4\pi c v X_p(c, l) l N_p \Lambda(l) dl \right) dc, \] or
\[ X(c) = \alpha N_p \int_{0}^{\infty} X_p(c, l) l \Lambda(l) dl, \] (4.10)
where \( \alpha = 4\pi c v \) [m²/s] is a proportionality constant that depends only on the measuring device settings.

If we consider particles to be compact structures characterized by a single density and having all the same shape, then by introducing the particle mass distribution (PMD) we can rewrite Eq. (4.10) in terms of mass as follows
\[ X(c) = \alpha N \int_{0}^{\infty} X_p(c, l(m)) l(m) M(m) dm, \] (4.11)
where \( m \) is the mass of the particle and \( M(m) \) represents the PMD normalized to 1. The relationship between particle's characteristic size and its mass \( l(m) \) can be derived
by expressing the mass as follows

\[ m = \rho V = \rho \int dV = \rho \int_S \frac{h}{3} \frac{da}{3} \]

\[ = \rho \int_S \frac{|s(u, v) \cdot (T_u \times T_v)| |T_u \times T_v|}{|T_u \times T_v|} \frac{\partial u \partial v}{3} \]

\[ = \rho \frac{1}{3} \int_S |s(u, v) \cdot (T_u \times T_v)| \partial u \partial v = \rho \frac{1}{3} lS, \]

here \( \rho \) represents the particle density, \( V \) its volume and the differential volume \( dV \) was chosen as a cone whose base is a particle surface element and its vertex is the particle center of mass as detailed in Fig. 4.3. Multiplying and dividing by \( l^2 \) we can further simplify Eq. (4.12) as follows:

\[ m = \rho l^3 f_X, \text{ with} \]

\[ f_X = \frac{1}{3 l^2} \frac{S}{3} \frac{\left( \int_S |s(u, v) \cdot (T_u \times T_v)| \partial u \partial v \right)^4}{\left( \int_S |s(u, v) \cdot (T_u \times T_v)| \partial u \partial v \right)^2}, \]

where \( f_X \) is a factor depending only on particle shape. To demonstrate it let us scale particle’s size by a factor \( \xi \) so that the new particle surface equation is \( s'(u, v) = \xi s(u, v) \)

and its tangent vectors become $T'_u = \xi T_u$ and $T'_v = \xi T_v$, respectively, then

$$f'_x = \frac{1}{3} \left( \frac{\int_y |\xi T_u \times \xi T_v| \, \partial u \, \partial v}{\int_y |s(u, v) \cdot (\xi T_u \times \xi T_v)| \, \partial u \, \partial v} \right)^4 =$$

$$= \frac{1}{3} \left( \frac{\int_y |T_u \times T_v| \, \partial u \, \partial v}{\int_y |s(u, v) \cdot (T_u \times T_v)| \, \partial u \, \partial v} \right)^4 = f_x. \quad (4.15)$$

Eq. (4.13) ultimately leads to the following integral relationship between PMD and CLD

$$X(c) = \alpha \rho^{-1/3} \beta \chi \int_0^{\infty} X_p(c, l(m)) m^{1/3} M(m) \, dm, \quad (4.16)$$

where $\beta = f_{x_1}^{-1/3}, \; \lambda(m) = \beta \chi \rho^{-1/3} m^{1/3}$ and $X_p(c, l(m))$ is the CLD of a monodisperse distribution of particles of mass $m$.

### 4.4 Relationship between CLD moments and PSD and PMD moments

#### 4.4.1 Size Scaling: The Scaled CLD

As indicated at the beginning of the treatment of the CLD of particles of any shape, we considered only particles having the same shape and whose geometry could be described by a single parameter, $l$. Two of such particles are shown in Fig. 4.4. The vertical straight line represents one of the possible trajectories the laser beam can follow. We can say that the two particles have the same shape because we can obtain the particle in Fig. 4.4(b) by scaling the particle in Fig. 4.4(a) by means of a scale factor, $\xi$ such that each chord length $c$ also scales by the same factor so that we can write

$$X_p(c, l) \, dc = X_p(\xi c, \xi l) d(\xi c) \Rightarrow X_p(c, l) = \xi X_p(\xi c, \xi l),$$

by setting $\xi = l^{-1}$ we obtain

$$X''_{p}(c/l) \equiv X_p(c/l, 1) = lX_p(c, l),$$
where the scaled single particle CLD, $X'_p(c/l)$ represents the CLD of a particle of unit size and it is a function only of the particle shape and not of its size. Thus the definition of a new variable $\chi \equiv c/l$ enables us to write the fraction of cuts in $[c, c+dc]$ as follows

$$X_p(c, l)dc = lX_p(c/l, 1)d(c/l) = X_p(c/l, 1)d(c/l) = X'_p(\chi)d\chi.$$ 

We can then conclude that by scaling the chord length by the characteristic size of the particle the fraction of cuts in $[c, c+dc]$ can be written in a way that depends only on the particle shape. This result will be used in the following sections to separate the effects of shape and size.
4.4.2 Number of particles and average characteristic length

The \( j \)-th moment of the CLD, PSD and PMD are respectively defined as follows:

\[
\mu_j^c = \int_0^\infty c^j X(c) \, dc,
\]

\[
\mu_j^l = \int_0^\infty l^j \Lambda(l) \, dl,
\]

\[
\mu_j^m = \int_0^\infty m^j M(m) \, dm.
\]

Combining Eq. (4.10) and Eq. (4.17) we can write

\[
\mu_j^c = \alpha N_p \int_0^\infty \left[ \int_0^\infty c^j X_p(c, l) \, dc \right] l^j \Lambda(l) \, dl
\]

\[
= \alpha N_p \int_0^\infty \left[ \int_0^{\infty} \frac{c^j}{l^{j+1}} X_p(c, l) \, dc \right] l^{j+1} \Lambda(l) \, dl
\]

\[
= \alpha \mu_j^c N_p \int_0^\infty l^{j+1} \Lambda(l) \, dl,
\]

thus obtaining the following final relationship between CLD moments and PSD moments:

\[
\mu_j^c = \alpha \mu_j^c N_p \mu_{j+1}^l.
\]

where \( \mu_j^c \) is defined as the \( j \)-th moment of the scaled single particle CLD, where chords have been scaled by means of \( l \) as defined in Eq. (4.8), and depends only on particle shape.

If we write Eq. (4.20) for \( j = -1 \) we can express \( N_p \) in terms of CLD moments as follows:

\[
N_p = \frac{\mu_{-1}^c}{\alpha \mu_{-1}^l}.
\]
In light of what just derived Eq. (4.20) can be solved for $\mu_{j+1}^l$

$$
\mu_{j+1}^l = \frac{\mu_{j-1}^\gamma \mu_{j}^\varepsilon}{\mu_{j}^\gamma \mu_{j-1}^\varepsilon}, \tag{4.22}
$$

Sometimes also useful are the so-called moments about the mean:

$$
\tilde{\mu}_i = \int_0^\infty (l - \mu_1^l)^i N(l) \, dl, \tag{4.23}
$$

which are related to raw moments through the following relationship

$$
\tilde{\mu}_i = \sum_{k=0}^i \binom{i}{k} (-1)^{i-k} \mu_k^l (\mu_1^l)^{i-k}, \tag{4.24}
$$

combining the last relationship with Eq. (4.22) yields

$$
\tilde{\mu}_i = \sum_{k=0}^i \binom{i}{k} (-1)^{i-k} \mu_{k-1}^\gamma (\mu_1^l)^{i+1-k} \frac{\mu_{k-1}^\gamma (\mu_0^l)^{i-k}}{(\mu_{i-1}^\gamma)^{i+1-k}}. \tag{4.25}
$$

Using previous equation for $i = 2$ we obtain the following expression for the standard deviation of the PSD

$$
\sigma = \sqrt{\frac{\mu_{i-1}^\gamma}{\mu_{i-1}^\varepsilon}} \sqrt{\frac{\mu_{i}^\varepsilon}{\mu_{i}^\gamma} - \mu_0^\varepsilon}. \tag{4.26}
$$

Recapitulating Eqs. (4.21), (4.22) and (4.26) enable us to extract important information about the PSD, and in particular any of its moments, from the measured CLD moments. The results show that the number of particles scales as the -1 order CLD moment while the characteristic average sizes of order $j$ scales with the ratio between the $(j - 1)$-th and the $-1$-th CLD moments.

### 4.4.3 Particle Structure

If we take in consideration the particle structure we can relate mass distributions to size distributions and consequently CLD moments to PMD moments. If we model particle
structure with a single particle density we can use Eq. (4.16) and Eq. (4.17) as follows

\begin{align*}
\mu_j^\xi &= \alpha \beta_\chi \rho^{-1/3} N_p \int_0^\infty \left[ \int_0^\infty \chi^j X_p(c, l(m)) dc \right] m^{1/3} M(m) \, dm \\
&= \alpha \beta_\chi \rho^{-1/3} N_p \int_0^\infty \left[ \int_0^\infty \left( \frac{c}{l(m)} \right)^j l(m) X_p(c, l(m)) dc \right] \times \\
& \quad \times l(m)^j m^{1/3} M(m) \, dm \\
&= \alpha \beta_\chi \rho^{-1/3} N_p \int_0^\infty \left[ \int_0^\infty \chi^j X_p^\prime(\chi) d\chi \right] \beta_\chi^\xi \rho^{-1/3} m^{j+1/3} m^{1/3} M(m) \, dm \\
&= \alpha \beta_\chi^{j+1} \mu_j^\xi \rho^{-(1+j)/3} N_p \int_0^\infty m^{(1+j)/3} M(m) \, dm,
\end{align*}

which results in the following relationship between mass and chord length based moments

\begin{equation}
\mu_j^\xi = \alpha \beta_\chi^{j+1} \mu_j^\xi \rho^{-(1+j)/3} N_p \mu_{\xi-1}^{m}, \tag{4.27}
\end{equation}

which rewritten in order to express PMD moments in terms of CLD moments yields

\begin{equation}
\mu_i^m = \frac{\rho^j}{\alpha \beta_\chi^{3i} N_p \mu_{\xi-1}^{m}} \mu_j^\xi, \tag{4.27'}
\end{equation}

By taking \( j = 2 \) in Eq. (4.27) an expression for \( \rho \) is obtained

\begin{equation}
\rho = \alpha \beta_\chi^3 \mu_2^\chi (N_p \mu_1^m) \frac{1}{\mu_2^\xi}. \tag{4.28}
\end{equation}

where \( N_p \mu_1^m \) is constant since it represents the total mass per unit volume in the system. Consequently under this assumption particle density inversely scales with the second order CLD moment.
4.5 Application of the Moment Relationship to the Measured CLD

4.5.1 Sizing of Particles of Unknown Shape

Interpretation of CLD measurement in terms of Sizes for particles of unknown shape

Our objective is that of sizing particle populations of unknown shape. Yet we have to wonder what is the size of an object of any given shape. For a spherical object the answer is straightforward since a sphere is uniquely identified by only one parameter, namely the radius. A non spherical object, though, cannot be characterized by one parameter. In general, an infinite number of parameters are to be provided through a three dimensional parameterized surface representation. In order to distinguish between shape and size it is not unusual to define a characteristic length of an object (such as for example the maximum distance of a surface point from the center of mass or the radius of a sphere having the same volume) which is then used to scale the parameterized surface, as it has been done for example in Fig.4.4. In this manner the shape is represented by the scaled parameterized surface and the size is represented by the characteristic length. It is important to note, however, that the choice of the characteristic length is completely arbitrary. This implies that if we compare the size of two objects of different shape according to a certain definition of characteristic length we might well obtain a result that differs from that originating by another definition.

When particle sizing is concerned, it is the measuring principle employed that dictates the definition of the characteristic length, in this perspective then the particle size is an operationally defined quantity. Actually in the more general case the measuring principle also dictates how the contribution of each particle is weighted. For example in dynamic light scattering [21] the intensity weighted diffusion coefficient is measured, and the application of the Stokes-Einstein relationship results in the so called average hydrodynamic radius. This quantity can be interpreted as the radius of the sphere whose diffusion coefficient is equal to the measured average diffusion coefficient.

Going back to the FBRM measurements it is important to note that this technique is inherently unidimensional as opposed for example to image analysis which is bidimen-
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Consequently, it is certainly not possible to obtain from these measurements information about both particle size and particle shape. Then the question that one would naturally pose is: what can we measure through FBRM when we don't know the shape?

Let us first assume that we knew the particle shape, then the characteristic length $l$ is defined as of Eq. (4.8) and its average value $\mu_j^{l+1,j} = \mu_j^{l+1,j}/\mu_j^l$ using Eq. (4.22) takes the following expression

$$\mu_j^{l+1,j} = \frac{\mu_{j-1}^l \mu_j^l}{\mu_j^l \mu_{j-1}^l}.$$  (4.29)

Thus knowledge of the shape factors $\mu_j^l$ enables us to straightforwardly calculate $\mu_j^{l+1,j}$ from the measured CLD. Based on this line of thought one might conclude that in FBRM measurements $l$, as defined in Eq. (4.8), is the only size we can obtain. This conclusion is nevertheless incorrect since we are ignoring that we know a priori the particle shape, indeed based on this knowledge we could obtain any alternatively defined size. In practical situations, however, we generally don't know the shape and we cannot calculate the shape factors, therefore the previous procedure cannot be applied. Then how do we obtain the size or better how do we define the size in order to obtain it from a FBRM measurement? In the following we propose two different approaches we can take in order to attack this problem.

In analogy to dynamic light scattering data processing we assume the particles to be spherical and we calculate the corresponding shape factors $\mu_j^{l,s}$ (c.f. Appendix 4.A) and based on Eq. (4.22) we define the average measured size of order $j$ as follows

$$\mu_j^{l,s} = \frac{\mu_{j-1}^{l,s} \mu_j^{l,s}}{\mu_j^{l,s} \mu_{j-1}^{l,s}}.$$  (4.30)

The size just defined can be interpreted, similarly as in dynamic light scattering, as the average radius of a population of spheres distributed in such a way to exhibit a CLD equal to the measured CLD.

Alternatively we could consider the total particle surface per unit volume $N_pS$ and the total particle length per unit volume $\mu_j^l N_p$, which both can be expressed as a function
of only moments of the CLD [86]:

\[ SN_p = \frac{8\mu_1^p}{\alpha}, \quad (4.31) \]

\[ \mu_1^p N_p = \frac{\mu_0^p}{\alpha}, \quad (4.32) \]

the latter originating form Eq. (4.20) with \( j = 0 \). It is worth noting that the two relationship do not include any shape factors. Division of Eq. (4.31) by Eq. (4.32) naturally leads to definition of the following average size

\[ \frac{S}{\mu_1^p} = 8\frac{\mu_1^p}{\mu_0^p}. \quad (4.33) \]

At first sight this definition would seem shape independent since, as opposed to Eq. (4.29), it does’t contain any shape factor. However this is not true because dependency on shape is hidden in the definition of \( S \) and \( \mu_1^p \). It should be readily noticeable that the second approach leads to an expression which is equivalent but for a multiplicative constant to Eq. (4.29) evaluated at \( j = 1 \).

The Case of the Thin Rod with Variable Aspect Ratio

We want to evaluate the behavior of the size definitions given in the previous section as the shape of the particles under examination changes. One of the simplest three-dimensional geometrical figures that, as opposed to the sphere, allows for shape changes is the cylinder. Indeed different ratios of the height \( \bar{l} \) to the base radius \( r \) yield different shapes according to the definition given in the previous section. In Appendix 4.B the single particle CLD \( X_p^c(c, \bar{l}, r) \) for a thin cylinder of height \( \bar{l} \) and radius \( r \) with \( r \ll \bar{l} \) is derived analytically together with an expression for the characteristic length \( \bar{l}^c \) as defined in Eq. (4.8). As we are not interested in the effects of the polydispersity of the size distribution we will consider hereafter only monodisperse populations. In order to avoid cumbersome integrals of \( X_p^c(c, \bar{l}, r) \) originating from Eq. (4.29) we prefer to use the characteristic size definition (4.33), that is the ratio between the particle surface area \( S^c = 2\pi r \bar{l} + 2\pi r^2 \) and the characteristic size \( \bar{l}^c \) as given by Eq. (4.46).

Fig. 4.5(a) shows this quantity divided by \( 8\pi \) as a function of the base diamenter, \( r \) for \( \bar{l} = 20 \) (dotted line), \( \bar{l} = 25 \) (dashed line) and \( \bar{l} = 30 \) (dash-dotted line) while the solid line represents the diagonal. It appears that in the case of the thin cylinder the
Figure 4.5: (a) Average size as defined in Eq. (4.33) versus base diameter, \( r \) for different values of cylinder's height \( \bar{l} \). (b) Characteristic size, \( l^e \) as defined in Eq. (4.8) versus base diameter, \( r \) for different values of cylinder's height \( \bar{l} \).

measured size, as we have defined it, scales as the radius of the cylinder base. This at first sight contrasts with the fact that the characteristic length \( l^e \) mainly scales with cylinder's height as it is readily seen in Eq. (4.46) and shown in Fig. 4.5(b). Indeed a deeper analysis reveals that the second observation simply tells us that for a thin cylinder the dominant dimension is its height. As a direct consequence cuts are more likely to happen in a direction orthogonal to it due to how single particle CLD are weighted. Therefore the major part of the recorded chords length will be equal to the dimension orthogonal to the axis of the cylinder, which happens to scale as the base radius. This ultimately explains why we measure the smallest dimension in an object that has one dominant dimension.

More generally we can say that, owing to the single particle CLD weighting, the average sizes as we have defined them are biased towards the characteristic lengths orthogonal to the dominant dimension. Thus FBRM will not be able to monitor any process that involves the growth along a single preferred dimension, such as for example crystal epitaxial growth. This analysis allows us to conclude that as long as the particles are not strongly anisotropic and their shape is not strongly changing in time, the proposed methodology of interpretation of FBRM measurements will be able to deliver a reasonable representation of the kinetics of change of the average size of the particulate system.
The application of what presented so far to real measurements requires the ability to properly transform the measured data into moments of the CLD. As mentioned in § 4.2 the raw data provided by the measuring device consists of \( n - 1 \) counts \( X_i \) of the cuts falling within the chord interval \([c_i, c_{i+1}]\) where \( \{c_i\} \) with \( i \in \{1, \ldots, n\} \) is a predefined chord grid. This information is evidently not the CLD required to calculate its moments, although a simple method for obtaining them would be that of dividing the counts by the corresponding interval length thus yielding the following approximate piecewise constant representation of the CLD

\[
X(c) = \frac{X_i}{c_{i+1} - c_i}, \quad i : c \in [c_i, c_{i+1}].
\] (4.34)

Under certain circumstances, however, this might result in a poor approximation of the true CLD and correspondingly a poor approximation of its moments. Therefore a more refined solution has to be sought.

A more careful analysis of the measured raw data reveals that the counts \( X_i \) can be expressed as follows

\[
X_i = \int_{c_i}^{c_{i+1}} X(c)dc, \quad i \in \{1, \ldots, n - 1\}
\] (4.35)

which summed up from 1 to \( j - 1 \) leads to:

\[
\hat{X}_j = \sum_{i=1}^{j-1} X_i = \int_{c_1}^{c_j} X(c)dc = \int_0^{c_j} X(c)dc, \quad j \in \{1, \ldots, n\},
\] (4.36)

which is nothing else than the cumulative chord length distribution (CCLD) \( \hat{X}(c) \) evaluated at \( c_j \). This means that what is actually measured in FBRM is not the CLD but the CCLD evaluated at the predefined grid-points\(^2\). Indeed the CLD has to be derived from the discretized CCLD provided by the measurement. This can be done by approximating the true CCLD through a suitable interpolation of the measured CCLD points. Then, owing to their mutual relationship, a simple derivative of the approximated CCLD will yield the desired approximated CLD. In light of this discussion it is evident that the method for obtaining the CLD from the experimental data given by Eq. (4.34)

\(^2\)In the following we will include \( c_1 = 0 \) as first grid-point since here the CCLD is obviously equal to 0.
corresponds to approximating the measured CCLD with the following piecewise linear function

\[ \hat{X}(c) = \hat{X}_i + \frac{X_i}{c_{i+1} - c_i} (c - c_i), \quad i : c \in [c_i, c_{i+1}], \]  

(4.37)

which is obtained connecting adjacent measured points.

If we want to improve on Eq. (4.34) we must find an approximation of the CCLD better than piecewise linear functions. Owing to the fact that we have to take a derivative of our approximation the choice naturally falls on spline approximation [88]. A piecewise cubic approximation of the CCLD looks as follows

\[ \hat{X}(c) = a_i c^3 + b_i c^2 + d_i c + e_i, \quad i \in \{1, \ldots, n-1\} : c \in [c_i, c_{i+1}], \]  

(4.38)

a third order spline approximation is obtained when \( \hat{X}(c_i) \) equals the measured points, \( \hat{X}(c) \) has first and second order derivatives continuous in \([0, c_n]\) and when suitable end-conditions are provided in 0 and \( c_n \). These requirements allow for the calculation of all the coefficient appearing in Eq. (4.38) from the measured data. From the derivative of Eq. (4.38) the approximated CLD is obtained

\[ X(c) = 3a_i c^2 + 2b_i c + d_i, \quad i \in \{1, \ldots, n-1\} : c \in [c_i, c_{i+1}], \]  

(4.39)

which in turn enables us to calculate the CLD moment of order \( j \) as follows\(^3\)

\[ \mu_j = \int_0^\infty c^j X(c)dc = \sum_{i=1}^{n-1} \int_{c_i}^{c_{i+1}} c^j X(c)dc, \]

\[ = \sum_{i=1}^{n-1} 3a_i \left( c_i^{3+j} - c_i^{3+j} \right) + 2b_i \left( c_i^{2+j} - c_i^{2+j} \right) + d_i \left( c_i^{1+j} - c_i^{1+j} \right). \]  

(4.40)

To test the performance of the two data treatment methods (4.34) and (4.39) against each other we used a FBRM unit model D600L (Lasentec, 15224 NE 95th Street, Redmond, WA 98052, USA) to measure the CLD of the PVC suspension at 8.33% mass fraction that is provided with the unit itself as a calibration reference sample. The measurement, performed using the “C” setting for the unit which discriminates real counts from noise,

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\(^3\)For \( j = -3, -2, -1 \) the formula can be obtained as limit for \( j \to -3, -2, -1 \) of the general formula.
lasted 60 seconds while the chord grid used was geometrical spanning the interval 1μm – 1000μm in 90 bins which corresponds to a grid factor $\zeta_0 \simeq 1.08$. After the raw data were collected the corresponding CCLD was calculated by means of Eq. (4.36). The data were then resampled from the original grid factor to a different grid factor $\zeta$ in order to test the effect of grid coarsening on the CCLD, the CLD and the CLD moments evaluated through the piecewise linear approach and the spline approach, respectively. The resampling was performed by generating a spline interpolation of the original CCLD and subsequently using it to generate the CCLD on the new grid. To illustrate an example of grid coarsening, Fig. 4.6 shows the result of both piecewise linear and spline CCLD approximation for the original data resampled to a geometrical chord grid made up of 9 bins whose corresponding grid factor is $\zeta \simeq 2.154$. More in detail in Fig. 4.6(a) the spline approximated CCLD given by Eq. (4.38) with the data on the original grid (90 bins) is shown (dash-dotted line) together with the spline approximated CCLD given by Eq. (4.38) with the resampled data (9 bins) (solid line) and the piecewise linear approximated CCLD given by Eq. (4.37) with the resampled data (dotted line). Circles represent the resampled data point. Considering that the spline approximation of the original data provides the most accurate CCLD, and in fact in Fig. 4.6(a) it would not be
distinguishable from the original data, it is evident the better approximation provided by the spline method on the coarser grid with respect to the piecewise linear function. It should be noticed however that, as the inset better illustrates, for such an extremely coarse grid an oscillation in the spline approximation at high chords can appear. This issue would be even more severe if we imposed the more commonly used zero second order derivative as right end-condition instead of zero derivative in the development of the spline approximation Eq. (4.38). In Fig. 4.6(b) the CLDs corresponding to the CCLDs shown in Fig. 4.6(a) are shown. It is important to notice that the CLDs obtained through spline approximation do not vanish at c equal to zero. This is so because we chose to set zero second order derivative as left end-condition. Apart from the apparent better performance of the spline method, it should also be observed that for such a coarse grid the oscillation in the spline approximation of the CCLD shown before results in negative values of the CLD for high chords.

![Figure 4.7: Percentage error ε versus grid factor ζ for spline approximation (4.40) (circles) and for piecewise linear approximation (squares). Lines are plotted to guide the eye.](image)

In order to assess the effect of grid coarsening on the CLD moments estimated either through spline approximation or through piecewise linear approximation we calculated, starting from the same raw data considered above, the average size \( \mu_{2,3}^\varepsilon \) defined by Eq. (4.30) as a function of the grid factor, and computed the following percentage devi-
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Fig. 4.7 shows the resulting plot for both the approximation methods. When the grid is fine enough both methods yield the same performance. As the grid coarsens the error in the piecewise linear method steadily increases while the spline method results in no appreciable error until the grid factor reaches a value of roughly 1.5 that corresponds to circa 20 bins. This values will in general depend on the particular measuring setup used which dictates the noise level of the measured signal as well as on the shape of the particular CLD under examination. These observations unequivocally demonstrate the superiority of the spline approximation method in evaluating the CCLD, the CLD and its moments. The advantage in the use of coarse grid lies in the fact that, keeping the noise constant, one can decrease the duration of the measurement. In such in-situ on-line technique this is clearly a very important result, particularly when monitoring processes characterized by fast dynamics.

4.6 Conclusions

A detailed mechanistic model for FBRM particle detection of objects of an arbitrary convex shape was developed. As a result the convolution relationship relating CLD to PSD and CLD to PMD were obtained. For the first time the exact expression for the shape dependent characteristic length scale appearing as weight in the aforementioned convolution relationships was given. Based on this rigorous results we could derive relationships between CLD moments and PSD moments which introduce shape dependent multiplicative factors. Equivalent relationships between CLD and PMD moments allowed us to provide a new relationship for the density of particles expressed in terms of measured CLD moments. This for example can be useful in flocculation monitoring where aggregation, breakage and restructuring can lead to changes in particle structure. Moreover for systems with constant density this relationship showed that the total mass scales as the inverse of the second moment of the measured CLD. A detailed discussion about the interpretation of size distribution in particulate systems of variable shape and its relationship with the experimental technique used was presented. Hence building upon previous modeling results, specifically the moment relationships, we proposed
method for defining a size in terms FBRM measurements. The analytical expression
for the CLD of a thin cylinder was derived and used as a model particle of variable
shape. In order to bring insight into the role of the characteristic weighting length as
opposed to the measured size, we showed that the FBRM technique, due to its measuring
principle, is not well suited for monitoring processes that involve growth mainly along
a single spatial direction. On the other hand we have also shown that for moderately
anisotropic particles that retain their aspect ratio during the process FBRM provides
valuable quantitative information on the average size of the particulate system under
examination.

4.1 Moments of the scaled CLD for Spheres

For a sphere, the single particle CLD reads [82]

\[
X_p^s(c) = \begin{cases} \frac{c/(2l)^2}{\sqrt{1-(c/2l)^2}} & \forall c \in [0, 2l[ \\ 0 & \forall c \in [2l, \infty[ , \end{cases}
\]

where the characteristic dimension \( l \) is taken to be the radius. Consequently the scaled
single particle CLD is expressed as follows

\[
X_p^{s'}(\chi) = \begin{cases} \frac{\chi^4}{\sqrt{1-\chi^2/4}} & \forall \chi \in [0, 2[ \\ 0 & \forall \chi \in [2, \infty[ , \end{cases}
\]

and its \( j \)-th order moment becomes

\[
\mu_j^{s'} = \int_0^\infty \chi^j X_p^{s'}(\chi)d\chi = \frac{2^{j-3}\sqrt{\pi} \Gamma \left( \frac{2+j}{2} \right)}{\Gamma \left( \frac{3+j}{2} \right)},
\]

where \( \Gamma(x) \) is the gamma function.

The relevant values of \( \mu_j^{s'} \) are

\[
\mu_{-1}^{s'} = \frac{\pi}{4}, \quad \mu_2^{s'} = \frac{8}{3}, \quad \mu_0^{s'} = 1, \quad \mu_1^{s'} = \frac{\pi}{2}, \quad \ldots
\]
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4.B Derivation of the CLD for the Thin Cylinder

Here we want to derive an expression for the single particle CLD $X_p^\infty(c)$ of a cylinder of base radius $r$ and height $l$ valid in the limit $r/l \ll 1$. We have first to specify its position relative to the moving laser beam. In order to do this let us consider a frame of reference where the laser beam is orthogonal to the $xy$ plane and sweeps in a plane parallel to the $xz$ plane. The said relative position is then given by placing the center of mass of the cylinder in the origin of the frame of reference and specifying the orientation of the cylinder itself. The last piece of information is provided by the angle $\phi$ formed by the projection of the cylinder's axis onto the $xy$ plane and the $x$ axis, together with the angle $\theta$ formed by the cylinder axis and the $z$ axis. Fig. 4.8 illustrates these concepts.

Arguments similar to those leading to Eqs. (4.8) and (4.7) enable us to write the following expression for the product of the cylinder's characteristic length, $l^c$ and the corresponding
single particle CLD, $X'_p(c)$

$$I^c X'_p(c) = \int X_p(c, \phi, \theta) l'(\phi, \theta) dn.$$  \hspace{1cm} (4.42)

Here $X_p(c, \phi, \theta)$ is the CLD along the $x$ axis of the contour of the projection of the semicylinder onto the $xy$ plane (solid rectangle in Fig. 4.8), $l'(\phi, \theta)$ is the maximum extension of the contour itself along the direction of the $y$ axis as shown in Fig. 4.8 and $dn$ is the differential fraction of cylinders whose orientation falls within $[\phi, \phi + \partial \phi] \times [\theta, \theta + \partial \theta]$. The last term is actually equal to the corresponding differential solid angle $\sin \theta \partial \theta \partial \phi$ divided by the solid angle subtending the whole space. Consequently Eq. (4.42) becomes

$$I^c X'_p(c) = \int \int X_p(c, \phi, \theta) l'(\phi, \theta) \frac{1}{4\pi} \sin \theta \partial \theta \partial \phi.$$ \hspace{1cm} (4.43)

Our problem is therefore reduced to that of calculating $X_p(c, \phi, \theta)$ and $l'(\phi, \theta)$. To solve it we must consider three different cases.

In the first case, the laser beam cuts the only lateral surface of the cylinder. This happens when $\phi > \phi^*$ and $\theta > \theta^*$ where $\phi^*$ and $\theta^*$ are expressed as follows

$$\phi^* = \arcsin \left( \frac{r}{l/2 \sin \theta} \right) \approx \frac{r}{l/2 \sin \theta}, \hspace{1cm} \theta^* = \arcsin \left( \frac{r}{l/2} \right) \approx \frac{r}{l/2}.$$ 

Fig. 4.9 shows the contour of the projection of the semicylinder onto the $xy$ plane (green solid line) as it looks in first case. The thick solid segment represents one of the infinitely many possible cuts in this configuration. From the drawing it is evident that all these cuts have the same length $2r/|\sin \phi|$ thus resulting in the following expression

$$X_p(c, \phi, \theta) = \delta(c - 2r/|\sin \phi|).$$

From the cartoon is also evident that $l'(\phi, \theta) = l/2 |\sin \theta \sin \phi|$.

In the second case the orientation is such that the semicylinder is almost contained in the $xz$ plane but it is not orthogonal to the $xy$ plane. This translates into the fact that $\phi < \phi^*$ and $\theta > \theta^*$. In this situation the laser beam starts cutting the base of the semicylinder, then travels along the lateral surface parallel to its axis ending the cut.

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4The cylinder obtained by cutting in correspondence of the center of mass.
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Figure 4.9: Projection onto $xy$ plane of the thin cylinder.

when the opposite base is reached. This means that we can write

$$X_p(c, \phi, \theta) = \delta(c - \bar{l} \sin \theta), \quad l'(\phi, \theta) = r.$$ 

In the last situation the semicylinder is almost orthogonal to the $xy$ plane whatever be the value of the angle $\phi$. This happens when $\theta < \theta^*$ and the result is that the laser will see only the base of the semicylinder so that we can easily write

$$X_p(c, \phi, \theta) = X_p^*(c, r), \quad l'(\phi, \theta) = r.$$ 

The results obtained for each of these three cases enables us to split the integral in Eq. (4.43) into three contribution as follows

$$l^*X_p^*(c) = 8 \int_{\phi^*}^{\phi^*} \int_{\phi^*}^{\phi^*} \partial \phi \delta(c - 2r / \sin \phi) \frac{\bar{l}}{2} \sin \theta \sin \phi \frac{\sin \theta}{4\pi} +$$

$$+ 8 \int_{\phi^*}^{\phi^*} \partial \phi \delta(c - \bar{l} \sin \theta) r \frac{\sin \theta}{4\pi} +$$

$$+ 8 \int_0^{\phi^*} \partial \phi \int_0^{\phi^*} X_p^*(c, r) \frac{\sin \theta}{4\pi},$$

where, exploiting the feature that due to the symmetry of the system the result is the same for each octant, we have restricted the integrals to the first octant and multiplied the result by 8. In addition, this allowed us to drop all the absolute values appearing in the derivations of $X_p(c, \phi, \theta)$ and $l'(\phi, \theta)$. Straightforward but laborious solution of
the integrals appearing in the previous equation leads to the following expression for $l'\chi_p(c)$:

$$l'\chi_p(c) = \begin{cases} 
\frac{1}{2\sqrt{4r^2 - c^2}} \left(1 - \sqrt{1 - \left(\frac{2r}{l}\right)^2}\right) & \forall \ c \in [0, 2r[ \\
\frac{1}{\pi} \frac{(\frac{2r}{l})^2}{\sqrt{1 - \left(\frac{2r}{l}\right)^2}} + \frac{1}{2\pi} \frac{\frac{2r}{l}\sqrt{1 - \left(\frac{2r}{l}\right)^2 + \arccos\left(\frac{2r}{l}\right)}}{\frac{2r}{l}\sqrt{\left(\frac{2r}{l}\right)^2 - 1}} & \forall \ c \in ]2r, l[ \\
0 & \forall \ c \in [l, \infty[.
\end{cases} \tag{4.45}$$

Since $X_p(c)$ is normalized to 1 we have

$$l' = \int_0^\infty l'\chi_p(c)dc = \frac{l}{4} + r \left[1 - \sqrt{1 - \left(\frac{2r}{l}\right)^2} + \frac{r}{\pi} \left(1 - \frac{4}{\pi} \arcsin\left(\frac{2r}{l}\right)\right)\right]. \tag{4.46}$$

The last formula eventually enables us to calculate $X_p(c)$ from Eq. (4.45).
5 Aggregation of Concentrated Polymer Latex in Stirred Vessels

5.1 Introduction

A sizeable amount of polymeric materials are produced via emulsion polymerization due to its inherent thermal control, high productivity even for high molecular weights and moderate viscosity increases \[4, 5\]. Another advantage of emulsion polymerization resides in the colloidal nature of the final product. Due to its physical properties the final latex can be used “as such” in many applications such as for example paints, coating and finishes. On the other hand, when the application requires the polymeric material in powder form, a process for separating the polymer from water has to be set up.

At colloidal sizes Brownian motion effectively suppresses the tendency of the polymer particles to sediment due to its density difference with the suspending medium. Consequently, a stable latex, in which polymer particles effectively repel each other, shows a negligible tendency to phase separate. When the stabilization mechanism is removed, Brownian motion and macroscopic velocity gradient can cause polymer particles to collide and stick together due to van der Waals attraction, thus leading to aggregates of larger size. Such aggregation process \[30\] eventually brings about sedimentation due to the system’s loss of colloidal character, thus leading to phase separation. Accordingly, aggregation appears to be a viable route in the setup of an industrial process for separating the solid phase from water in polymeric latices.

Several methods for imparting colloidal stability exist. One of the most commonly adopted relies on electrostatic repulsion forces. In this stabilization mechanism an amphiphilic ionic species is added to the dispersion so that, by adsorbing at the polymer particle surface, a surface charge is developed. As a result a repulsive interparticle Coulomb force arises, providing stabilization by preventing particle collisions. When a strong electrolyte is added to an electrostatically stabilized latex, the ions effectively
screen the existing surface charge, colloidal stability is lost and consequently particles aggregate. The aggregation rate strongly increases upon increasing electrolyte concentration. Above the critical coagulation concentration (CCC) repulsion forces are completely screened and the aggregation rate reaches a constant value where the process becomes diffusion limited. Accordingly, a typical industrial process for separating the polymer phase from water in an electrostatically stabilized latex is based on mixing a salt solution with the latex in an agitated vessel operated in batch or continuous mode. It is commonly chosen to work in fully destabilized conditions, i.e. at salt concentrations above CCC, in order to avoid the aforementioned strong dependency of the aggregation rate upon salt concentration, consequently favoring the productivity and the robustness of the process. In these conditions the aggregation process becomes very fast thus competing with the mixing process typical of stirred vessels, and leading to gels even in the presence of substantial breakage.

The complex interplay among these processes is not investigated in the literature covering salt induced aggregation of electrostatically stabilized latices in agitated vessels [12-20], where the aggregation process was significantly slowed down by operating at extremely low particle volume fractions. In addition, the particle size of the latices used in the aggregation experiments is normally above 1 micron, which is far bigger than the particle sizes in typical industrial latices, which are of the order of hundred nanometers.

In this work we address these issues by performing suitable experiments in a stirred vessel with fully destabilized latices of a small particle size in concentrated conditions, which are the conditions typical of industrial applications. By monitoring on-line and in-situ the time evolution of the size distribution of the polymer aggregate dispersion, we can derive information about the competition between aggregation, breakage and the mixing processes. These are relevant aspects in the design of a coagulation unit since the aggregate size distribution is one of the main characteristics in determining the value of the final polymer powder. The importance of these considerations can be better appreciated when considering that in a typical coagulation unit aggregates of average size of the order of 100-500 \( \mu \text{m} \) are produced starting from latices of primary particles whose size is of the order of 100 nm. This corresponds to a scale-up factor of 3 to 4 orders of magnitude.
5 Aggregation of Concentrated Polymer Latex in Stirred Vessels

5.2 Theoretical Aspects

5.2.1 Aggregation and Breakage in Stirred Vessels

Aggregation and breakage of colloidal aggregates in ideal stirred vessels can be modeled by means of the following population balance for the \( k \)-fold aggregate (i.e. an aggregate containing \( k \) primary particles) known as the Smoluchowski coagulation equation \[7\]

\[
dN_k \over dt = \frac{1}{2} \sum_{i+j=k} K_{ij}N_i(t)N_j(t) - N_k(t) \sum_i K_{ki}N_i(t) - \Gamma_k N_k(t) + \sum_i \Gamma_i \Delta_{ik} N_i(t),
\]

(5.1)

where \( N_i(t) \), \( N_j(t) \) and \( N_k(t) \) are the number concentrations of the \( i \)-fold, \( j \)-fold and \( k \)-fold aggregate at time \( t \), respectively. The first two terms on the right hand side represent the effect of aggregation and the last two represent the effect of breakage. The matrix of second order aggregation rate constants \( K_{ij} \), usually referred to as the aggregation kernel, reflects the physics of the aggregation process. The breakage rate is described using a first order kinetic model \[16\] where \( \Gamma_k \) is the corresponding rate constant for a aggregate of mass \( k \), which generally depends on aggregate size and turbulent intensity, while \( \Delta_{ik} \) represents the fraction of fragments of mass \( k \) originating from the disruption of a aggregate of mass \( i \) and is usually referred to as the daughter distribution function. In fully destabilized conditions, as those considered here, it is reasonable to assume \[89\] the aggregation kernel to be expressed by the sum of two contributions, \( K_{ij}^{\text{Brown}} \) and \( K_{ij}^{\text{Turb}} \), due to Brownian motion and turbulent flow, respectively. For collisions of aggregates of sizes \( R_i \) and \( R_j \) their expressions read \[7,90\]

\[
K_{ij}^{\text{Brown}} = 4\pi(R_i + R_j)(D_i + D_j),
\]

(5.2)

\[
K_{ij}^{\text{Turb}} = \sqrt{\frac{8}{15}} \sqrt{\frac{\epsilon}{\nu}} (R_i + R_j)^{3},
\]

(5.3)

where \( \epsilon \) is the rate of turbulent energy dissipation, \( \nu \) is the suspending medium kinematic viscosity and \( D_i \) and \( D_j \) are the aggregates diffusion coefficients. The diffusion coefficient of an \( i \)-fold aggregate can be expressed by means of the Stokes-Einstein relation as follows

\[
D_i = \frac{k_BT}{6\pi\mu\beta R_i},
\]

(5.4)
where \( k_B \) is the Boltzmann constant, \( \beta \) is a constant of order one accounting for the shape of the aggregate and \( \mu \) is the suspending medium viscosity. In order to close the model (5.1) to (5.4) an expression relating the aggregate size to its mass, based on some assumption about its structure, has to be provided. In the case of pure Brownian aggregation, it has been shown [91] that such a relationship for an aggregate made up of \( i \) particles is given by

\[
i = k_0 \left( \frac{R_i}{a} \right)^{d_f},
\]

where \( d_f \simeq 1.8 \) is the fractal dimension, \( k_0 \) is a constant of order one and \( a \) is the primary particle radius. This result is known as fractal scaling. Since the scaling indicates that the aggregate density decreases with size, at some point of their growth space will be filled and gelation occurs [92], thus resulting in one single aggregate spanning the whole system.

In the case of semibatch operation where a salt solution above CCC and a stable polymeric latex with particle number concentration \( N'_k \) are fed into the system at volumetric feed rates \( Q_S \) and \( Q_L \), respectively. Eq. (5.1) is modified as follows

\[
\frac{dN_k}{dt} + \frac{N_k(t) \frac{dV}{dt}}{V(t)} = \frac{Q_L}{V(t)} N'_k + \frac{1}{2} \sum_{i+j=k} K_{ij} N_i(t) N_j(t) + \Gamma_k N_k(t) + \sum_i \Gamma_{ik} \Delta N_i(t),
\]

where the total volume of the system, \( V(t) \), is a function of time and can be obtained by writing a suitable mass balance on the whole system. It is to be noted that, in writing the equations above, we have tacitly assumed that aggregation and breakage are slow compared to mixing, and that the stirred vessel can be regarded as a uniform system with respect not only to composition, but also to the energy dissipation rate.

### 5.2.2 Timescales of Mixing and Aggregation

Let us consider a stream of stable latex at solid volume fraction \( \phi_F \) entering an agitated vessel containing a salt solution at a concentration well above CCC. As the latex volume enters the system it is stretched and folded by the turbulent motion of the salt solution. At the same time salt molecules diffuse into it through its boundaries. As time elapses.
the stretching and folding mechanism will impart a lamellar structure to the volume itself [93], thus increasing its surface area and decreasing its characteristic length scale. This process lasts until a length scale is attained where salt molecular diffusion becomes effective and the mixing at smaller scales is complete. Let us call the characteristic time of this process \( \tau_M \). It should be noticed that \( \tau_M \) refers to the salt, while the polymer particles, whose diffusion coefficient is smaller by at least two orders of magnitude, certainly exhibit a larger mixing time.

In this frame we can consider that, as the local salt concentration in the latex volumes (whose disruption is controlled by mixing) increases, colloidal stability is lost and aggregation becomes significant. Due to the strong sensitivity of the aggregation rate to the salt concentration, it can be safely assumed that aggregation is very slow until the CCC is reached. However at the CCC and above, the characteristic time of aggregation \( \tau_A \) can be either smaller or larger than \( \tau_M \). In the case \( \tau_A \ll \tau_M \), the aggregation process would take place before mixing is complete. This has the important consequence that, since salt molecules diffuse at a far larger rate into the latex volume than the polymer particle into salt volumes, aggregation mainly occurs at volume fractions very near the feeding volume fraction \( \phi_F \). This tends to be substantially large and therefore can easily lead to gelation. As a consequence, at very high feed solid volume fractions gelation can freeze in latex volumes into gel aggregates whose size is dictated by the extent of the reduction of the initial latex volume caused by turbulent mixing which was reached at the time where gelation occurred. On the other hand, if \( \tau_A \gg \tau_M \) aggregation occurs uniformly in the entire vessel, which means also very low aggregate concentrations thus making the gelation process more unlikely. It is clear that the final powder obtained in the two cases might end up being very different in terms of both particle structure and aggregate size distribution (ASD).

In order to assess the likelihood of the above scenario let us evaluate the aggregation, gelation and mixing timescales based on simple models of aggregation and turbulent mixing available in the literature. In the above conditions the initial aggregation rate corresponds to the aggregation of primary particles whose aggregation rate constant \( K_{11} \) can be derived from Eqs. (5.2) and (5.3) as follows

\[
K_{11} = \frac{8k_BT}{3\mu} + 8\sqrt{\frac{8}{15}\pi} \sqrt{\frac{\varepsilon}{\nu}} \alpha^2. \tag{5.7}
\]

Considering that aggregation follows a second order kinetics in particle number concen-
5 Aggregation of Concentrated Polymer Latex in Stirred Vessels

tration, \( N_F \), the corresponding aggregation characteristic time \( \tau_A \) is given by

\[
\tau_A = \frac{1}{K_{11} N_F} = \left( \frac{2k_B T}{\pi \mu a^3 \phi_F} + \frac{6}{\pi} \sqrt{\frac{8}{15}} \sqrt{\frac{\epsilon}{\nu \phi_F}} \right)^{-1},
\]

(5.8)

where the particle number concentration has been expressed in terms of the solid volume fraction as \( N_F = 3\phi_F/(4\pi a^3) \) and it was assumed, according to the above discussion, that aggregation at the very beginning takes place at the particle concentration value in the feed stream. On the other hand, if the time required by the turbulent flow to reduce the characteristic lengthscale of the feed to the Kolmogorov microscale is very short, \( \tau_M \) is on the order of the smallest timescale of a turbulent flow, namely the Kolmogorov timescale \( \tau_n \) [94]:

\[
\tau_M \approx 17\tau_n = 17\sqrt{\frac{\nu}{\epsilon}}.
\]

(5.9)

In order to evaluate the relative magnitude of the two characteristic times, the contour plot of the logarithm of the ratio of the characteristic time of mixing \( \tau_M \) to the characteristic time of aggregation \( \tau_A \), \( \tau_M/\tau_A \) is shown in Fig. 5.1. The range of particle sizes and volume fractions typically explored in the literature under shear aggregation conditions (\( 10^{-5} < \phi < 10^{-3} \) and \( 0.8 \mu m < a < 2 \mu m \)) (refs. [12 20]) is represented by the crosshatched area. It can be seen that these conditions correspond to \( \tau_M/\tau_A \approx 10^{-2} \), so that it is safe to assume that aggregation occurs on a timescale long enough to avoid mixing effects on the aggregation kinetics. On the other hand, if we consider conditions typical for industrial applications (hatched area in Fig. 5.1), i.e. small particle radii (for example, in the case of polymeric latices, in the range between 40 and 150 nm) and high volume fractions (say larger than 0.1), the situation radically changes and the aggregation is mixing-controlled. In these conditions, the aggregation timescale is at least one order of magnitude smaller than that of mixing. This arises because smaller particles have higher diffusion coefficients thus enhancing aggregation, and higher volume fractions imply higher particle number concentrations that in turn lead to smaller aggregation characteristic times, since aggregation follows second order kinetics.

Let us now bring into this frame also the gelation process. Since for small particles turbulent shear aggregation is negligible compared to Brownian aggregation, we use a simple model of Brownian aggregation to estimate the characteristic timescale of gelation.
5 Aggregation of Concentrated Polymer Latex in Stirred Vessels

Figure 5.1: Contour plot of the logarithm of the ratio $\tau_M/\tau_A$ between the characteristic time of micromixing and the characteristic time of aggregation as a function of primary particle radius and solid volume fraction in the latex. Labels represent the value of the logarithm corresponding to the isoline. Values of the parameters used for the computations: $T = 298$ K, $\epsilon = 0.1$ W/kg, $\mu = 8.91 \cdot 10^{-4}$ Pa/sec $\nu = 8.91 \cdot 10^{-7}$ m$^2$/sec.

$\tau_G$: In static conditions the Smoluchowski coagulation equation reads

$$\frac{dN_k}{dt} = \frac{1}{2} \sum_{i+j=k} K_{ij} N_i(t) N_j(t) - N_k(t) \sum_i K_{ki} N_i(t), \quad (5.10)$$

where the aggregation kernel can be expressed using Eq. (5.2) and Eq. (5.4) as follows

$$K_{ij} = K_{ij}^{Brown} = \frac{2k_B T}{3\mu} \left( \frac{1}{R_i} + \frac{1}{R_j} \right).$$

In Brownian DLCA aggregation, as time elapses, the mass distribution remains fairly monodisperse, consequently as a first approximation it can be described using the constant kernel $K_{ij} = 8k_B T/3\mu$ [91]. This leads to the following expression for the number concentration of the average aggregates $N_k$

$$\frac{dN_k}{dt} = -\frac{8k_B T}{3\pi\mu} N_k^2(t) = -\frac{1}{\tau_A} \frac{N_k^2(t)}{N_F}. \quad (5.11)$$

where the subscript $k$ indicates the mass of the average aggregate in the system. Con-
servation of mass requires that

\[ N_k \frac{dN_k}{dt} = N_F, \quad \frac{dN_k}{N_k} = -\frac{N_F}{k^2} \frac{d\bar{k}}{dt}, \]

which allows us to recast Eq. (5.11) in terms of \( \bar{k} \) as follows

\[ \frac{d\bar{k}}{dt} = \frac{1}{\tau_A}, \quad (5.12) \]

thus leading to the following expression of the average aggregate size as a function of time:

\[ \bar{k}(t) = 1 + t/\tau_A. \quad (5.13) \]

Once we can predict the time evolution of the average mass, it is necessary to define a proper criterion for gelation, so as to obtain an estimate of \( \tau_G \). Among the simplest gelation criteria is the one that identifies the occurrence of colloidal gelation as the time when the fraction of the volume occupied by the aggregates is of the order of 1 [45]:

\[ \frac{4}{3} \pi R_k^3 N_k(t = \tau_G) \approx 1, \quad (5.14) \]

where \( R_k \) is the average radius of the aggregates in the system. Accordingly, by means of Eqs. (5.13) and (5.5) we can give the following estimation of \( \tau_G \)

\[ \tau_G \approx \tau_A \left( \frac{d_f}{\phi_F \frac{d_f}{d_f^*}} - 1 \right). \quad (5.15) \]

A typical value for \( d_f \) in fully destabilized conditions is about 1.8 [91], and from Eq. (5.15) we can see that in the range of \( \phi_F = 0.1 - 0.3 \) the ratio \( \tau_G/\tau_A \) takes values roughly between 5 and 30. It follows that in conditions where \( \tau_M/\tau_A \gg 1 \) the characteristic time of gelation can well be of the same order or smaller than \( \tau_M \). Thus we can conclude that in conditions where aggregation is mixing controlled, such as those typical of industrial operations, it is very likely that in a very small latex volume, whose disruption is governed by mixing, the aggregates grow several orders of magnitude in size and eventually gelate, so that the entire volume is occupied by a single aggregate.
5.2.3 Focused Beam Reflectance Method

Focused beam reflectance method (FBRM) allows for convenient online and in-situ monitoring of particulate systems up to very high solid content, especially if compared with scattering techniques. The measurement device consists of a tubular probe which can be inserted directly into the vessel. A highly focused rotating laser beam illuminates the system through a sapphire window located at the tip of the probe. When the path of the laser beam crosses a particle with sufficient optical contrast with respect to the suspending medium, the backscattered light is collected through the same sapphire window. From this and the knowledge of the laser rotational speed, the length of the path traveled by the laser across the particle can be calculated. This task is performed by the electronic discrimination circuit of the device, which analyzes the backscattering signal spanning the measurement time and sorts the traced path length into chord bins so as to give as output the so-called chord length distribution (CLD) of the polymer particles [80, 81]. To within a proportionality constant (depending only on aggregate shape and structure), moments of the CLD can be transformed into moments of the ASD as follows [95]

\[ \mu^I_{j+1} = \alpha_j \frac{\mu^C_j}{\mu^C_{-1}} \]  

(5.16)

where \( \mu^I_i \) represents the \( i \)-th moment of the ASD, \( \mu^C_j \) the \( j \)-th moment of the CLD and \( \alpha_j \) is a proportionality constant depending on \( j \) and on the aggregate structure. Eq. (5.16) was used to extract the following weighted averages of the ASD from the measured CLD

\[ d_{4,3} = \frac{\mu^4_3}{\mu^3_3}, \quad d_{1,0} = \frac{\mu^1_0}{\mu^0_0}, \]

which for a spherical shape read

\[ d_{4,3} = \frac{32 \mu^S_5}{9\pi \mu^S_3}, \quad d_{1,0} = \frac{\pi \mu^S_0}{2 \mu^S_{-1}}. \]  

(5.17)
5.3 Experimental

The polymer latex used for the aggregation experiments was a PVDC dispersion type PV-324 provided by Solvay Solvin France S.A.. The primary particle diameter was found by dynamic light scattering (Zetasizer 5000, Malvern Instruments) to be 90 nm with a nearly monodisperse particle size distribution. Solid volume fractions were measured by gravimetry (HG53 Halogen Moisture Analyzer, Mettler Toledo). Throughout all the experiments demineralized water was used for required dilutions or salt solution preparations. Aluminum nitrate nonahydrate (Fluka) was used to induce aggregation. The corresponding CCC was estimated through static aggregation experiments to be \( \sim 0.02 \, \text{g/l} \).

The first series of aggregation experiments was performed in a jacketed stirred glass vessel (nominal volume 9 l) equipped with two Rushton turbines. Experiments were run as follows. The vessel was filled with two liters of foot solution of salt at concentration \( C'_S \) at a temperature of 5°C, which is below PVDC's glass transition temperature. While the stirrer was set to rotate at the desired speed \( S \), stock latex at volume fraction of \( \phi_F = 0.111 \) and temperature of 5°C and salt solution at concentration \( C'_S \) were fed into the system at flowrates \( Q_L \) and \( Q_S \), respectively, until the total volume of 8 liters was reached with the final volume fraction. Feeding was implemented by means of peristaltic pumps. The feeding pipe (internal diameter 3 mm) was placed vertically into the vessel. The pipe's outlet was positioned at the upper part of the discharge zone of the lowest impeller and in the middle between the vessel wall and the impeller tip. Weighting of the feed reservoir during the feeding process provided accurate measurements of the feed flowrates. \( Q_L \) and \( Q_S \) were chosen so as to reach the desired final volume fraction \( \phi \), whereas the value of \( C'_S \) was determined by requiring the coagulant concentration to be above the critical coagulation concentration (CCC) during the whole feeding process as detailed below. In all the experiments the feeding lasted 55 minutes and the system temperature was kept between 5°C and 10°C. After the feeding process was finished, the system was left to reach steady state. Jacket temperature was then set to 90°C and the vessel temperature reached 75-78°C. This was done to induce polymer crystallinity in order to impart desirable physical properties. The vessel was then cooled down by setting the jacket temperature to 25°C. Eventually, water was filtered out and the resulting wet powder was vacuum dried at 40°C.

Based on the procedure described above, once the final volume fraction, \( \phi \) and salt
Aggregation of Concentrated Polymer Latex in Stirred Vessels

Concentration, $C_S$ are chosen, all the remaining operating conditions can be calculated through the following material balances

$$Q_L \Delta t_F \phi_F = V_T \phi,$$

$$(Q_L + Q_S) \Delta t_F = V_T - V_F,$$

$$C'_S (\Delta t_F Q_S + V_F) = (1 - \phi) V_T C_S,$$

that solved for the unknowns $Q_L$, $Q_S$ and $C'_S$ lead to

$$Q_L = \frac{\phi V_T}{\phi_F \Delta t_F},$$

$$Q_S = \frac{V_T - V_F}{\Delta t_F} - Q_L,$$

$$C'_S = \frac{(1 - \phi) \phi_F}{\phi_F - \phi} C_S,$$

where $V_T$ and $V_F$ are the final and foot volumes, respectively, $\Delta t_F$ is the feeding time and for $C_S$ a value of 1 g/l was taken as a conservative choice so as to ensure that the salt concentration is always well above CCC. It can be readily seen that in this setup the latex feeding rate $Q_L$ is proportional to the final volume fraction $\phi$. This situation, which is representative of the operating mode of semibatch industrial coagulators, has the disadvantage that both the fluidodynamics conditions in the vessel and the aggregate concentration change simultaneously, thus making it difficult to decouple their effects. For this reason a second experimental set-up has been devised where these effects could be studied independently.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Series</th>
<th>$\phi \cdot 10^2$</th>
<th>$Q_L \cdot 10^2$ [l/min]</th>
<th>$Q_S \cdot 10^2$ [l/min]</th>
<th>$S$ [r.p.m.]</th>
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<td>410</td>
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<tr>
<td>3</td>
<td>A</td>
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<td>9.53</td>
<td>0.596</td>
<td>645</td>
</tr>
<tr>
<td>4</td>
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<td>0.106</td>
<td>9.98</td>
<td>165</td>
</tr>
<tr>
<td>5</td>
<td>C, B</td>
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</tr>
<tr>
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<td>C</td>
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<td>0.121</td>
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<td>1.28</td>
<td>0.92</td>
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Table 5.1: Operating conditions in the first experimental setup. In all the experiments the remaining operating parameters were fixed as follows: $\Delta t_F = 55$ min, $\phi_F = 0.111$, $V_T = 8$ l and $V_F = 2$ l

The second series of experiments was performed in a jacketed stirred glass vessel (nominal volume 6 l) equipped with one Rushton turbines. The vessel was operated full, so that
the liquid level always reached the upper metal flange so as to avoid the presence of air. This was achieved by pumping only latex at the desired volume fraction $\phi_F$ and feed flowrate $Q_L$ into the coagulator already full of salt solution above CCC. Water was allowed to flow out through a filtered outlet so as to keep the particles inside and the vessel always full. In all the experiments the system volume was 8.88 liters. The feeding process lasted until the final solid volume fraction, $\phi$ was reached. As soon as the feeding stage was over, the system was left to equilibrate before the heating procedure was performed, as in the previous experimental setup. The initial salt concentration in the vessel was calculated so as to give a salt concentration well above CCC at the end of the feeding process.

<table>
<thead>
<tr>
<th>Exp</th>
<th>Series</th>
<th>$Q_L \cdot 10^2$ [l/min]</th>
<th>$\phi \cdot 10^2$</th>
<th>$\phi_F \cdot 10^2$</th>
<th>$\tau_A$/M</th>
<th>$\tau_G$/M</th>
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</tr>
<tr>
<td>9</td>
<td>D</td>
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<td>0.23</td>
<td>1.40</td>
<td>174</td>
<td>0.01201</td>
</tr>
<tr>
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</tr>
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<tr>
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</tr>
<tr>
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<td>0.35</td>
<td>12.0</td>
<td>190</td>
<td>8.23</td>
</tr>
<tr>
<td>19</td>
<td>E</td>
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<td>0.35</td>
<td>12.0</td>
<td>190</td>
<td>8.23</td>
</tr>
<tr>
<td>20</td>
<td>E</td>
<td>2.95</td>
<td>0.35</td>
<td>12.0</td>
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<td>8.23</td>
</tr>
<tr>
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<td>9.22</td>
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</tr>
</tbody>
</table>

Table 5.2: Operating conditions in the second experimental setup. In all the experiments the remaining operating parameters were fixed as follows: $V_T = 8.88$ l and $S = 165$ r.p.m.

In all the experiments the aggregate size distribution was monitored on-line by means of the sensor Lasentec FBRM D600L (Lasentec, Redmond, WA), with electronic discrimination circuit set to "C" and the laser focus point left at the factory default, placed inside the vessel just above the discharge zone of the lowest impeller.
5.4 Results and Discussion

5.4.1 Experimental Results

![Figure 5.2: Snapshot of the latex feed entering the vessel at the very early stage of feeding. (a) Experimental run 17 of series E in Table 5.2. (b) Experimental run 22 of series E in Table 5.2.](image)

As a first experimental result it is convenient to consider the pictures in Fig. 5.2 which show the first instant of time where the latex is entering the salt solution inside the vessel through the vertical tube. Fig. 5.2(a) and Fig. 5.2(b) correspond to the experimental runs 17 and 22 of series E in Table 5.2, respectively, where the operating conditions, which are near to those of industrial interest, probably correspond to the smallest value of the ratio between the characteristic times of aggregation and mixing, $\tau_A/\tau_M$. The white plumes indicate that aggregation is so fast that, before the latex volumes can be broken down to the Kolmogorov scale, not only aggregation, but most likely gelation of the entire mass has occurred. This indicates that we are dealing with a process strongly affected by mixing at the small scales of turbulence, where therefore the conditions inside the vessel are not uniform. In particular, at least at the high volume fractions considered in Fig. 5.2, aggregation/gelation occurs almost instantaneously as the latex enters the vessel, and the rest of the process is then devoted to breaking down the so formed gel flocks. This has to be accounted for when interpreting the experimental results that we are going to discuss next.
First Experimental Setup

Figure 5.3: Experimental conditions of the experiments carried out in the first experimental setup. Dashed circles indicate the series to which each experiment belongs.

For what concerns the behaviour of the system in the first setup at steady state before the heating phase, as seen in Table 5.1, all the experiments were run at the same feeding volume fraction, \( \phi_F = 11.1\% \) and feeding time, \( \Delta t_F = 55 \text{ min} \). On the other hand, various values of the final volume fraction \( \phi \) and the stirring speed \( S \) have been investigated, while the flowrates, \( Q_L \) and \( Q_S \) have been changed according to Eqs. (5.18) and (5.19). Fig. 5.3 shows each experiment as a point in the \( \phi - S \) plane, where dashed circles indicate the series to which each experiment belongs. In series A the experiments were run at a moderately high final volume fraction of about 7.5\%, while three values of the stirring speed were investigated. Fig. 5.4(a) shows the measured volume weighted average diameter \( d_{4,3} \) (circles, left axis scale) and number weighted size (filled circles, right axis scale) as a function of the stirring speed, \( S \). It is seen that both average sizes are relatively insensitive to the variations of the agitation in the system. The situation radically changes for the experiments performed at a low final solid volume fraction of \( \phi \approx 9.5 \cdot 10^{-4} \), that is series C in Fig. 5.3. As shown in Fig. 5.4(b), in these conditions the increase of the stirring speed results in a marked decrease of both the volume and the number weighted sizes. This is consistent with results reported in the literature for dilute systems, where \( d_{4,3} \sim e^{-0.5} \) is often observed in turbulent conditions [96]. The
ratio of $d_{4,3}$ to $d_{1,0}$, which is a measure of the polydispersity of the size distribution, decreases from a value of 4.7 to 2.8 when $S$ changes from 165 to 645 r.p.m. This means that the decrease in size is accompanied by narrowing of the ASD. These observations indicate that, as the volume fraction in the system is increased from very diluted to concentrated conditions, a fundamental change in the aggregation/breakage mechanism occurs. While at high volume fractions the change in the aggregation rate due to the increase in the stirring speed seems to be balanced by a similar change in the breakage rate, this balance seems to no longer hold at low volume fractions.

In the series B of experiments we fixed the stirring speed at the intermediate value of 410 r.p.m. and let the final volume fraction change between the two values used in the previous two series. The results are shown in Fig. 5.5(a), where volume and number weighted sizes, $d_{4,3}$ are plotted against the solid volume fraction, $\phi$. It is seen that $d_{4,3}$ does not change significantly as the volume fraction increases and retains a value close to the smallest one measured in the previous series of experiments. On the other hand, the number weighted average size, $d_{1,0}$ decreases significantly as $\phi$ increases. This different behavior of $d_{4,3}$ and $d_{1,0}$ is consistent with an increase of the fraction of fines at higher solid volume fractions. However we should observe that, due to the specific characteristic of the adopted setup described above, the final volume fraction in the system is proportional to the latex feed flowrate. This means that, in the experiments
at higher final solid volume fractions, a larger feed flowrate has been used. Therefore, in these experiments we cannot decouple the effects of mixing and aggregate concentration. This issue is addressed in the second series of experiments where operating the vessel full and using a filter at the outlet allows us to decouple the feed rates from the final solid volume fraction in the system.

As far as the transient behavior of the system is concerned, it is interesting to compare the evolution of the cumulative chord length distribution (CCLD) measured in the experimental runs with low and high final solid volume fraction (i.e. low latex feed rate). In Fig. 5.6 the CCLDs measured at various times are reported for the experiments at \( \phi = 7.68 \cdot 10^{-2} \) and \( Q_L = 8.20 \cdot 10^{-2} \) l/min (Fig. 5.6(a)) and at \( \phi = 1.02 \cdot 10^{-3} \) and \( Q_L = 1.35 \cdot 10^{-3} \) l/min (Fig. 5.6(b)), i.e. experiments 2 and 5 in Table 5.1, respectively. It is seen that at the higher feed rate the aggregate population moves towards smaller chords as time passes by. Even after feeding is over, this trend continues until the equilibrium distribution is reached. In contrast, at the lower feed rate (Fig. 5.6(b)) the CCLD remains practically unchanged during feeding and equilibration. In this case the feeding process is so slow that at each instant in time an equilibrium between aggregation and breakage is reached, as it is also demonstrated by the fact that the distribution at the end of the equilibration stage perfectly falls atop of the earlier ones. We should
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Figure 5.6: Plot of the cumulative chord length distribution (CCLD) normalized to one at various percentages of the feeding time, \( \Delta t_F \): (a) Experiment 2, \( \phi = 7.68 \cdot 10^{-2} \) and \( Q_L = 8.20 \cdot 10^{-2} \) l/min; (b) Experiment 5, \( \phi = 1.02 \cdot 10^{-3} \) and \( Q_L = 1.35 \cdot 10^{-3} \) l/min.

also consider that in this experiment the final solid volume fraction, \( \phi \) is so low that the volume fraction in the system changes very little, which explains why the CCLD remains constant also during the feeding stage. On the other hand, in experiment 2 the volume fraction in the system changes substantially in time, thus the fact that the CCLD continues to move to the left even after the feeding is over until equilibrium is reached indicates that the system is not at steady state and the equilibration stage is further shifted to the left.

First Experimental Setup

In Table 5.2 the operating conditions used for the second experimental setup are reported. In all the experiments the stirring speed was fixed at 165 r.p.m. Fig. 5.7 shows each experiment as a point in the \( \phi_F - Q_L \) plane, and all the experiments may be classified into two series D and E, as indicated by the dashed circles. In series E, while keeping the feeding solid volume fraction, \( \phi_F \) close to 11%, the latex feed rate \( Q_L \) has been varied between 0.03 and 0.14 l/min, with a constant final solid volume fraction \( \phi \approx 1.3\% \). The corresponding measured volume weighted size \( d_{4,3} \) (open circles, left axis scale) and number weighted size \( d_{1,0} \) (filled circles, right axis scale) are plotted versus
Figure 5.7: Experimental conditions for the experimental series D and E carried out in the second experimental setup. Dashed circles indicate the series to which each experiment belongs.

$Q_L$ in Fig. 5.8(a). We can readily observe a significant decrease of the volume weighted size as $Q_L$ increases, but the effect of $Q_L$ on the number weighted size is insignificant. It follows that the ASD narrows down as $Q_L$ increases. It should be noticed that the experimental runs at the smallest flowrate are basically repetitions of the same experiment. It is seen that the reproducibility of the experiments is good, though the measured $d_{1.0}$ are somewhat more scattered.

Fig. 5.8(b) shows the results of the experiment series F in Table 5.2, where at fixed $Q_L$ and $\phi_F$ around 0.13 l/min and 28%, respectively, the effect of changes in the final solid volume fraction, $\phi$ on the measured average aggregate sizes has been studied. Note that larger values of the solid volume fractions, $\phi$ are reached in this case by operating the unit for longer times. Here we can observe that both average sizes decrease as the final volume fraction in the vessel increases, although the decrease in $d_{1.0}$ is less marked thus leading to narrower ASD.

In the last two series of experiments, i.e. E and F, the effects of the flowrate, $Q_L$ and the final solid volume fraction have been investigated independently. This can now help to explain the results of the series B of experiments in the first experimental setup, where these two parameters were coupled. In particular, we see that both of them...
Figure 5.8: Volume and number weighted average size in the second aggregation setup as a function feed flowrate (a) and final solid volume fraction (b). (a) Series E: $\phi \approx 1.3 \cdot 10^{-2}$, $Q_L \approx 0.11$. (b) Series F: $Q_L \approx 0.14$ l/min, $\phi F \approx 0.28$. Lines are drawn to guide the eye.

Independently produce the same qualitative effect on $d_{4,3}$ and $d_{4,3}$ as they did coupled together in the first setup. However it should be stressed that, as opposed to series B where the ratio $d_{4,3}/d_{4,3}$ markedly increased, in series E and F this ratio either remains constant or slightly decreases, respectively. This discrepancy can be explained if we take in consideration that series B was run at higher stirring speed, i.e. 410 r.p.m. instead of 165 r.p.m.. It, is in fact, most likely that in this series many big aggregates are broken by the agitation, and therefore an increase in $\phi$ and/or $Q_L$ yields no decrease in the volume weighted average size. This explanation is also supported by the observation that in series B $d_{4,3}$ is never larger than about 140 microns while in series E and F the same quantity can be as large as 300 microns.

In Fig. 5.9 the measured volume and number weighted average sizes are plotted against feeding volume fraction $\phi F$ for the data in series D. Here the final solid volume fraction was fixed at the smallest explored value, i.e. $\phi \approx 1.23\%$, while for the feed flowrate an intermediate value was chosen, i.e. $Q_L \approx 0.06$ l/min. We see that both sizes significantly grow as the feeding volume fraction increases over one order of magnitude until values typical of industrial operation are reached. Runs at the highest feeding volume fractions were essentially repetitions of the same experiment. As for series E we observe that reproducibility of $d_{4,3}$ is good while $d_{4,3}$ data are somehow scattered.
54.2 Interpretation of the Experimental Results

As discussed in the modeling section in the context of Fig. 5.1, for the operating conditions considered in this work we expect a substantial effect of the fluid dynamic conditions on the aggregation process. It is actually rather obvious that, if the process were not mixing controlled, no dependency other than that on the final solid volume fraction should be expected, while the data above show a significant dependence on the feed solid volume fraction and flowrate. In particular, the results reported for series D and E clearly demonstrate the interplay between mixing and aggregation. Another element supporting this statement is brought by the visual observation of the latex streams entering the vessel during an aggregation experimental run. In Fig. 5.2 two snapshots taken at the very beginning of the latex feeding process for the experimental runs 17 (Fig. 5.2(a)) and 22 (Fig. 5.2(b)) of series E in Table 5.2 are shown. We notice a white plume coming out of the feed pipe whose boundaries are frozen in by the gelation process and become millimeter sized aggregates. This indicates not only that aggregation is faster than mixing, but that even gelation occurs on timescales smaller than those of mixing at the local scales. A similar behavior was observed in all the experimental runs where the feed concentration was sufficiently high and/or the feed flowrate sufficiently low. In the opposite situation the plume boundaries are not frozen in by gelation and gradually fade as their lengthscale is further broken down by the mixing process. This behavior is illustrated in Fig. 5.10, where a snapshot taken at an early instant of time in
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Figure 5.10: Snapshot of the latex feed at very low solid volume fraction entering the vessel at the very early stage of feeding for the experimental run 8 of series D in Table 5.2.

the feeding process of a very diluted latex (experimental run 8 of series D in Table 5.2) is shown.

In order to quantitatively support these observations let us analyze the relevant timescales for our experimental conditions. Computational Fluid Dynamics (CFD) simulation enabled us to estimate the rate of energy dissipation in the vicinity of the feed point (see Appendix 5.A for details), and from this the corresponding value of the Kolmogorov microscale \( \eta \) at a stirring speed \( S = 165 \) r.p.m.:

\[
\eta \equiv \left( \frac{\nu^3}{\varepsilon} \right)^{1/4} \approx 50 \, \mu m.
\]

This value is below the average aggregate sizes observed in the experiments reported above, which suggests that mixing at scales larger than the Kolmogorov microscale (the so-called mesoscale) could play a role. On the other hand, it has been shown that the most active transient vortices involved in the process of micromixing have a typical size around \( 12\eta \) [97, 98] which in our case falls around 600 \( \mu m \) and is above the average sizes observed. This seems to indicate that both mixing mechanisms could affect the experimental reported here. Consequently we will consider both mechanism in the interpretation proposed in the following.

If we assume inertial convective disintegration of large eddies as the main mechanism acting in reducing the lengthscale of particle concentration fluctuation to the Kolmogorov
scale, then the corresponding mesomixing timescale is given by [97, 99]

$$\tau_{\text{meso}} = 2 \Lambda_c^{2/3} \varepsilon^{-1/3}$$  (5.21)

where $\Lambda_c$ is the characteristic lengthscale of the feed stream. If the linear velocity in the feeding pipe, $u_p$, is much larger than the average velocity near the feed point, $\bar{u}$ (jet conditions) $\Lambda_c$ is equal to half of the diameter of the pipe $d_p$ and the rate of energy dissipation $\varepsilon$ can be estimated as follows [100]

$$\varepsilon = \frac{u_p^3}{d_p}$$  (5.22)

In the opposite case (non-jet conditions) the momentum of the entering stream is very low and it instantaneously adjusts to the average velocity in the vicinity of the feed point, $\bar{u}$. An upper-bound approximation of $\bar{u}$ is given by the impeller tip velocity. In this case the characteristic length $\Lambda_c$ can be computed as the size of the stream that, at linear velocity $\bar{u}$, gives the feed flowrate $Q_L$, that is

$$\Lambda_c = \sqrt{\frac{Q_L}{\pi \bar{u}}}$$  (5.23)

In the conditions adopted in the series of experiments D and E the ratio $u_p/\bar{u}$ ranged from 0.1 to 0.43, and therefore we do not always have clear jet or non-jet conditions, particularly considering that estimating $\bar{u}$ by the impeller tip velocity can yield a value substantially greater than the real one. For this reason in the following we consider two values of characteristic mesomixing times: $\tau_{\text{meso}}^j$ and $\tau_{\text{meso}}^{nj}$, corresponding to jet and non-jet conditions as given by the following expressions

$$\tau_{\text{meso}}^j = \frac{2^{1/3} d_p}{u_p}$$  (5.24)

$$\tau_{\text{meso}}^{nj} = 2 \left( \frac{Q_L}{\pi \bar{u}} \right)^{1/3} \varepsilon^{-1/3}$$  (5.25)

respectively. In Fig. 5.11(a) the two mesomixing characteristic times are shown, together with the gel timescale $\tau_G$ given by Eq. (5.15), as a function of the feed solid volume fraction, $\phi_F$ for the experimental conditions corresponding to the series of experiments D in Table 5.2. It is seen that the two mesomixing times are quite similar and that for small feed volume fractions, $\phi_F$ the characteristic time of gelation, $\tau_G$ is orders of magnitude larger than the mesomixing time. However, as the feed solid volume...
fraction increases the gelation timescale decreases while the mesomixing ones remain constant, so that a crossover occurs at $\phi_F \approx 10\%$. This implies that at very small $\phi_F$ values, the latex stream entering the vessel has time to spread over the entire system volume before Brownian aggregation and subsequently shear aggregation start to be significant. In this case the system tends to be uniform and a dynamic equilibrium is then reached when the average aggregate size is large enough to bring about aggregate breakage. As the feed volume fraction is increased, Brownian aggregation gradually becomes faster than mixing, thus taking place at volume fractions larger than those that would be obtained if the latex would have been uniformly spread on the entire vessel through mixing. Hence gelation freezes in aggregates in a denser structure that enables them to better withstand shear stresses, leading to aggregate sizes larger than those obtained at the same final solid volume fraction, $\phi$ and smaller feeding volume fractions, $\phi_F$. This agrees with the measured aggregate sizes increasing with $\phi_F$ shown in Fig. 5.9. It should be noted that another physical phenomenon could play a role in the observed increase of the average size with the feed volume fraction. The fact that the mesomixing characteristic time is larger than the gelation characteristic time means that the turbulent flow has not enough time to bring the feed stream lengthscale, $\Lambda_c$.
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down to the Kolmogorov microscale by means of the stretching and folding mechanism. This implies that the final average aggregate size corresponds to the size reached by the feed stream lengthscale during the stretching and folding at the moment where gelation occurs and freezes in the aggregate structure. Obviously earlier gelation (which means higher \( \phi_p \)) will freeze in larger structures.

This last argument can be used also to explain the results observed in the experimental series E. Fig. 5.11(b) shows the corresponding gel timescale \( \tau_G \) and the mesomixing timescale in jet, \( \tau_{\text{meso}}^J \) and non-jet, \( \tau_{\text{meso}}^N \) conditions as a function of the feed flowrate \( Q_L \). Here we should stress that the estimate for the gelation characteristic time, \( \tau_G \), given in Eq. (5.15) neglects the contribution of shear to the aggregation. Since the shear aggregation rate scales with the volume of the aggregates (cf. Eq. (5.3)) this could lead to a substantially shorter gelation timescale. We see that while the mesomixing time in jet conditions decreases as the feed rate increases, the mesomixing time in non-jet conditions, instead, increases. In the former case larger \( Q_L \) values imply larger momentum values which lead to larger local energy dissipation rates (Eq. 5.22) and consequently shorter mixing times (Eq. 5.24). In the latter case larger feed flowrates produce larger characteristic lengths, \( \Lambda_c \) (Eq. 5.23) of the stream entering the vessel, which then takes more time to be reduced to the Kolmogorov microscale by the turbulent flow (Eq. 5.21). On the other hand, the aggregation/gelation characteristic time is not affected by the feed flowrate.

In this case it is obviously difficult to draw conclusions since, with the simple expressions used in this paper to describe mesomixing, we cannot sufficiently characterize the local fluidodynamics around the inlet of the feed stream. We can say a posteriori that, based on the arguments developed in the context of Fig. 5.11(b), the system should be better described by a jet model, since in this case as \( Q_L \) increases \( \tau_{\text{meso}}^J \) decreases, which means that the process of jet disruption is faster, and, since the gelation process takes always the same time, it follows that the aggregate size decreases as shown in Fig. 5.8(a). To further support this instance, it is useful to analyze the jets portrayed in Fig. 5.2. Fig. 5.2(b) shows the latex feed stream entering the vessel in one of the experimental runs at the highest feed flowrate explored in the second experimental setup, i.e. \( u_p/\bar{u} \approx 0.43 \). We notice that the latex flow is hardly affected by the flow field found in the vessel. Indeed, since the feed point is placed slightly above the discharge zone of the impeller, if the latex stream would adjust to the flow field in the vessel it should move horizontally slightly upwards. This corroborates our hypothesis that, at least at the highest feed
flowrates, the feed is in jet conditions. At the smallest feed flowrate explored, i.e. \( u_p / \bar{u} \approx 0.1 \), the situation is less clear as shown by the snapshot in Fig. 5.2(a). Here we notice that the length traveled by the latex stream following the direction of the feed pipe is substantially shorter than that in the previous case, even though it is not negligible as non-jet conditions would require.

In the discussion above we considered only the mixing process occurring on the mesoscale based on the observation that average aggregate sizes measured experimentally fall above the Kolmogorov scale calculated through CFD simulations. However, owing to the increase of viscosity caused by the suspended phase, the Kolmogorov scale could be actually larger than the given estimate. In this situation the mechanism of mixing due to energetically active small scale motions (i.e. the micromixing) is radically different from that acting on the mesoscale and discussed above. It is then worth then to discuss the experimental observations in the frame of micromixing. A widely adopted model for micromixing is the so-called Engulfment, Deformation, Diffusion (EDD) model [97, 98, 101, 102].

According to this model the main mechanism of micromixing is due fluctuating vorticity. Vortices engulf ambient fluid thus forming partially segregated laminae of initial size \( \eta \) which are stretched while diffusion transports chemical species across the laminae thus allowing for chemical reaction. When a time \( \tau_\omega \) is reached the vortices return to isotropy and new laminae are formed. This process repeats itself at a frequency \( \tau_\omega^{-1} \) while the number of laminae follows a geometric progression of ratio 2. The process lasts until reaction is complete. The size of the vortices is assumed to be \( \sim 12 \eta \) which corresponds to the shortest time to regain isotropy \( \tau_\omega \approx 12.7(\nu/\epsilon)^{1/2} \). Within this description of mixing at the small scales an important characteristic time is that of diffusion into a shrinking slab \( \tau_{DS} \) which is given by

\[
\tau_{DS} = 2 \left( \frac{\nu}{\epsilon} \right)^{1/2} \text{arcsinh}(0.05 \text{Sc}),
\]

where \( \text{Sc} = \mu_t / \rho D \) is the Schmidt number with \( D \) is the diffusion coefficient and \( \rho \) and \( \mu_t \) the density and viscosity of the suspension, respectively. When the Sc number is much smaller than 4000 and the diffusion coefficients of the chemical species are not substantially different engulfment becomes limiting and the EDD model can be further simplified into what is known as E-model [103]. The resulting characteristic micromixing timescale is then given by Eq. (5.9) and corresponds to the timescale of fluid engulfment. Within this description of micromixing we will have to accommodate salt diffusion from the engulfed lamellae into latex lamellae, aggregation/gelation and aggregate diffusion.
out of latex lamellae. It is important to stress that, as opposed to the case of standard chemical reactions, in our case the fluodynamic is affecting not only the mechanism of micromixing but also the aggregation rate equations. As a consequence interpretation of experimental results is less straightforward than in the case of chemical reactions.

In our situation, the Schmidt number for the salt falls well below 4000, therefore salt transport into the latex is limited by engulfment. This however doesn’t ensure that aggregation will occur in homogeneous conditions within the latex lamellae, indeed the salt concentration in the median plane of the lamella will reach the CCC after a time \( \tau_{DS,s} \) (given by Eq. (5.26) substituting the diffusivity of the salt) has elapsed since the lamella has been formed. In concentrated conditions this time might result longer than the characteristic time of aggregation, \( \tau_A \). This illustrated in Fig. 5.12 where several characteristic times related to micromixing and aggregation/gelation are plotted against the latex feed flowrate, \( Q_L \) for conditions corresponding to those of the series of experiments E. Here we notice that \( \tau_{DS,s} \) (solid line) is always bigger than \( \tau_A \) (dash-dotted line) as foreseen. This wouldn’t affect the final result if particle would diffuse out at the

![Figure 5.12: Characteristic times relevant to the interplay between micromixing and aggregation/gelation plotted versus the latex feed flowrate.](image)
same rate as the salt diffused in. However the dashed line in Fig. 5.12 shows that this is not the case since the characteristic time of primary particle diffusion across the lamella, \( \tau_{D,\mathrm{p}} \approx 2(\nu/c)^{1/2}\arcsinh(0.05 D_1/p\mu_c) \) is relatively bigger than \( \tau_{D,\mathrm{ss}} \). We should also note that, as particles aggregate and grow, their diffusion coefficient decreases thereby further substantiating the previous statement. The net result is that in our case the EDD model cannot be simplified to the E-model and consequently both the time of engulfment \( \tau_M \) and \( \tau_{D,\mathrm{p}} \) have to be considered in the interpretation of our experimental results.

As previously stated, we think that it is reasonable to assume that in the series of experiments E the latex feed stream is in jet conditions at least for high latex feed flowrates. Accordingly, we plotted in Fig. 5.12 the characteristic times for the case of jet stream. Always bearing in mind that the right value for the characteristic time of gelation, \( \tau_G \) might be smaller, we see that at low \( Q_L \) gelation is faster than aggregate diffusion across the slab. Hence the lamellae formed during salt engulfment and gelation are frozen to the size reached by stretching during this time span. As \( Q_L \) increases the rate of stretching of the laminae increases causing the gelation to freeze in smaller structures. Further increases the latex feed flowrate result in shorter aggregate diffusion times over the lamellae. Therefore at some point the aggregates are able to diffuse over the engulfment volume before gelation occurs and then aggregate in more dilute conditions most likely resulting in less denser structures. This interpretation is agreement with the initial decrease of the volume weighted average size observed in series of experiments E and reported in Fig. 5.8(a).

We should stress that the arguments given above are intrinsically of qualitative nature and therefore have to be used only as a guide for our understanding. For a quantitative interpretation of these results CFD tools coupled with suitable models of mixing at all the scales and a rigorous model for the aggregation/gelation process should be used. This is, however, beyond the scope of this experimental investigation.

For what concerns the effect of the final solid volume fraction, \( \phi \) illustrated in Fig. 5.8(b) the observed decrease of the average sizes is in contrast with what reported in Ref. [104], where the aggregation and breakage of polystyrene aggregates of 1 \( \mu \)m diameter in agitated vessels was studied and an increase in the average size was observed. However, it should be pointed out that, owing to the adopted light scattering sizing technique, the maximum explored solid volume fraction was about \( 2 \cdot 10^{-3} \) which is one order of magnitude smaller than the minimum value investigated in this work. In these conditions
mixing is presumably faster than aggregation and the system is then uniform. Accordingly, an increase of aggregate size with solid content would be justified owing to the fact that aggregation and breakage follow second and first order kinetics, respectively. Even if one would speculate that there exists a critical size above which the aggregation rate drops to zero due to inertial effects or to the fact that breakage events are correlated to aggregate encounters, still only a plateau would be justified, but not a decrease of the aggregate size as the one observed in Fig. 5.8(b). We must consider, though, that at high solid volume fractions such as those investigated in this work, the flow alteration of the continuous phase produced by one aggregate is felt by the others. The net result is that the viscosity of the suspension increases with volume fraction, so that for a given shear rate (or equivalently a stirring speed) the shear stresses acting on each aggregate increase with solid volume fraction [105]. This leads to an apparent order of the breakage kinetics which is larger than two and could justify the decrease of the aggregate size shown in Fig. 5.8(b).

In light of the discussion above, we can further analyze the transient behavior observed in the first experimental setup and illustrated in Fig. 5.6. Due to the high feed volume fraction, latex volumes entering the vessel are immediately aggregated and gelled into millimeter sized aggregates, which are subsequently broken to the equilibrium size. Since simple breakage is a first order process, its characteristic time is independent of volume fraction and remains constant as long as the stirring speed is kept fixed. As a consequence, the dynamics of the aggregate size distribution is controlled by the relative magnitude of the breakage characteristic time and the rate at which gel aggregates appear in the vessel, which is clearly proportional to the rate at which latex is fed into the vessel. In particular, for the large feed flowrate adopted in experiment 2 in Table 5.1, breakage is too slow compared to the rate at which gel aggregates are entering the vessel. Therefore, after stopping the feed, breakage is able to shift the aggregate size distribution towards smaller sizes, thus achieving the steady-state corresponding to the current conditions in the system as shown by the experimental data in Fig. 5.6(a). On the other hand, for the low feed flowrate used in experiment 5 in Table 5.1, breakage is sufficiently fast to achieve, at every instant, the same pseudosteady-state conditions which lead to the constant aggregate size distribution shown in Fig. 5.6(b). In this case of course no change occurs in the CCLD after stopping the feed.

A final confirmation of the analysis reported above comes from the scanning electron microscopy (SEM) pictures of the final aggregates collected for the experimental runs
4, 5 and 6 in Table 5.1, i.e. series C in Fig. 5.3, where at $\phi_F = 0.111$ the stirring speed increases from 165 r.p.m. to 645 r.p.m. We can observe very clearly the lamellar structure of the sample at the smallest stirring speed, which supports our understanding that the latex volume, after being stretched and folded, was frozen in the resulting lamellar shape by gelation. Subsequent moderate agitation in the vessel was not able to destroy the resulting structure. Upon increase of agitation it is evident that the same lamellar structure is gradually destroyed. It should be noted that these results indicate that the morphology of the aggregates is not affected by the softening of the polymer induced by the heating stage above the glass transition temperature. Most probably at the particular heat rate we imposed to the system, the softening could only act on length-scales smaller than those of the mixing layers before hardening due to crystallization became significant.

5.5 Conclusions

By means of very simple relations based on the relevant characteristic times the kinetics of micromixing and of aggregation and gelation for fully destabilized polymer latices in stirred vessels have been investigated. It is shown that, in industrially relevant conditions (i.e. volume fractions above 10% and primary aggregate sizes below 200 nm), latices aggregate and even gel before mixing at small scales is complete. These conditions have been investigated experimentally by feeding an electrostatically stabilized PVDC latex in a stirred vessel operated in a semibatch mode together with a salt solution with concentration above the critical coagulation concentration (CCC). During aggregation the temperature was always kept below PVDC glass transition temperature. The aggregate size distribution was monitored in-situ and online by means of the focused beam reflectance method.
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In a first experimental setup the salt solution and the latex at 11.1% volume fraction were fed into the system over a fixed time interval. At high volume fractions the steady state aggregate size was shown to be quite insensitive to the stirring speed. The opposite behavior was observed when the experiments were run at lower solid volume fractions. This observation suggests that a profound change in the aggregation/breakage mechanism occurs as the volume fraction in the system increases. Although this setup reproduces the conditions of the typical industrial coagulation unit, it has the disadvantage that both the fluidodynamics (due to the filling in time of the vessel) and the solid volume fraction change continuously during the process.

To avoid this, a second experimental setup has been designed where the three main operating variables: feed flowrate, feed solid volume fraction and final solid volume fraction in the vessel, can be investigated independently. The interpretation of the obtained results is based on the interaction between aggregation/gelation and mixing at small scales. Both mesomixing and micromixing were considered. Care was taken to properly account for the peculiarities of aggregation as opposed to standard fast chemical reaction. A simple estimation of the relevant characteristic times shows that aggregation/gelation and mixing at the small scales are the two competing processes, as it is also confirmed by the plume of gelled latex formed immediately after the entrance of the feed stream in the vessel. The general trend is that when gelation is faster than mixing at intermediate and small scales, the latex volumes gel before the surrounding turbulent flow can break them down to either the Kolmogorov in the case of mesomixing, or to scales small enough to allow for diffusion in the case of micromixing. The final size of the aggregates is then determined by the competition between the two processes. They tend to be larger the faster gelation can freeze in the latex volume and the slower mixing breaks them through the turbulent stretching and folding mechanism. This conclusion is supported by the scanning electron microscope images of the final aggregates. In the case of the fastest gelation times, i.e. at large feed solid volume fractions, they still exhibit a lamellar structure resembling the shape of the fluid folding during mixing at the outlet of the feed pipe. Due to the relative similarity between the micro- and mesomixing time most probably both mechanism play a role on the experimental observations. However, considering the approximations involved in the estimation of the relevant characteristic times, these conclusions have to be regarded as qualitative.
5. A Computational Fluid Dynamics Estimation of the Scales of Turbulence

To estimate the values of turbulent energy dissipation rate the Computation Fluid Dynamics (CFD) simulations were performed. In our simulations the standard $k - \epsilon$ model of turbulence was used [106,107]. This model was combined with standard wall function to resolve the near-wall region. The viscosity was set to that of water at 25°C. In order to sufficiently resolve the flow inside the vessel a mesh composed of circa 350000 cells with particular attention to intense shear and mixing regions was used. For that purpose several refining steps of the mesh near the important regions (impeller and feeding pipe) were performed, which leads to a cell size of around 200 $\mu$m in this regions. This size was at least one order of magnitude smaller then the integral scale of turbulence [97]. The value of the turbulent kinetic energy used for estimation of the value of aggregation kernel, Kolmogorov microscale as well as mesomixing timescale (if is controlling by the flow inside the stirred tank) was based on the $\epsilon$ value in the fluid volume which lies in the region approximately one pipe diameter from its end. The Estimated value of the Kolmogorov microscale $\eta$ at a stirring speed $S = 165$ r.p.m was: $\eta \approx 50\mu$m. Since the presence of the aggregates on the studied process could have significant effect on the fluid flow and consequently on turbulent energy dissipation rate, we performed also simulations where the viscosity was increased 10 time of the original value. The obtained values of the Kolmogorov microscales were approximately 4-5 times larger then those obtained for the original viscosity of water at 25°C. On the other hand, the turbulent energy dissipation rate increase around 50% of the value calculated for original case with water at 25°C.

Notation

- $a =$ Primary particle diameter
- $d_{4,3} =$ Volume weighted average aggregate size
- $d_{1,0} =$ Number weighted average aggregate size
- $d_p =$ Feeding pipe diameter
$D = \text{Diffusion coefficient}$

$D_i = \text{Diffusion coefficient an aggregate of non-dimensional mass } i$

$C_S = \text{Salt solution concentration in the system}$

$C_S' = \text{Salt solution feed concentration}$

$i = \text{Non-dimensional mass of an aggregate}$

$j = \text{Non-dimensional mass of an aggregate}$

$k = \text{Non-dimensional mass of an aggregate}$

$k_0 = \text{Prefactor in fractal scaling (Eq. (5.5))}$

$k_B = \text{Boltzmann constant}$

$K_{ij} = \text{Aggregation kernel matrix}$

$K_{ij}^{\text{Brown}} = \text{Brownian aggregation kernel matrix}$

$K_{ij}^{\text{Turb}} = \text{Turbulent aggregation kernel matrix}$

$N_i = \text{Number concentration of an aggregate of non-dimensional mass } i$

$N_i^F = \text{Number concentration of an aggregate of non-dimensional mass } i \text{ in the feed stream}$

$Q_L = \text{Latex volumetric feed rate}$

$Q_S = \text{Salt solution volumetric feed rate}$

$R_i = \text{Size of an aggregate of non-dimensional mass } i$

$S = \text{Impeller rotational speed}$

$Sc = \text{Schmidt number}$

$t = \text{Time}$
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\[ T = \text{Temperature} \]
\[ \bar{u} = \text{Average velocity near the feed point} \]
\[ u_p = \text{Linear velocity in the feeding pipe} \]
\[ V, V(t) = \text{Volume of the system} \]
\[ V_F = \text{Foot salt solution volume} \]
\[ V_T = \text{Final total volume in the vessel} \]

**Greek letters**

\[ \alpha_j = \text{Proportionality constant between CLD and ASD moments (Eq. (5.16))} \]
\[ \beta = \text{Hydrodynamic parameter appearing in the Stokes-Einstein relationship (Eq. (5.4))} \]
\[ \Gamma_k = \text{First-order breakage rate constant} \]
\[ \Delta_{nk} = \text{Daughter aggregate mass distribution} \]
\[ \Delta t_F = \text{Feeding duration} \]
\[ \epsilon = \text{Rate of turbulent energy dissipation} \]
\[ \eta = \text{Kolmogorov microscale} \]
\[ \Lambda_c = \text{Characteristic lengthscale of the feeding stream} \]
\[ \mu = \text{Suspending medium viscosity} \]
\[ \mu_j^s = j\text{-th order moment of the CLD} \]
\[ \mu_j^l = j\text{-th order moment of the ASD} \]
\[ \mu_s = \text{Suspension viscosity} \]
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\[ \nu = \text{Suspending medium kinematic viscosity} \]

\[ \rho = \text{Suspension density} \]

\[ \tau_{\text{meso}}^j = \text{Characteristic time of mesomixing in jet conditions} \]

\[ \tau_{\text{meso}}^{nj} = \text{Characteristic time of mesomixing in non-jet conditions} \]

\[ \eta = \text{Kolmogorov timescale} \]

\[ \tau_A = \text{Characteristic time of aggregation} \]

\[ \tau_{\text{DS}} = \text{Characteristic time of diffusion across a shrinking slab} \]

\[ \tau_{\text{DS,s}} = \text{Characteristic time of diffusion of salt ions across a shrinking slab} \]

\[ \tau_{\text{DS,p}} = \text{Characteristic time of diffusion of primary particles across a shrinking slab} \]

\[ \tau_G = \text{Characteristic time of gelation} \]

\[ \tau_M = \text{Characteristic time of mixing} \]

\[ \tau_\omega = \text{Characteristic time vortex return to isotropy} \]

\[ \phi = \text{Solid volume fraction in the system} \]

\[ \phi_F = \text{Feed solid volume fraction} \]
6 Conclusions

In this thesis the aggregation polymeric latices in stirred vessels has been studied in the case of high solid volume fractions. In order to characterize the colloidal stability of polymeric latices a novel general procedure for the reliable estimation from light scattering measurements of the rate of doublet formation has been introduced. Such a procedure is based on a suitable transformation of the measured quantity so that the resulting quantity is expected to grow linearly versus time in the initial phase of aggregation. The slope of the straight line interpolating the transformed experimental data yields an estimate of the doublet formation rate constant. The proposed procedure was then applied to the characterization of the colloidal stability at different volume fractions of a styrene-HEMA latex prepared by surfactant free polymerization. Then the same methodology was adopted for the characterization of the colloidal stability of polystyrene latices stabilized by SDS and aggregating in a slow regime. The doublet formation rate constant measured at different ionic strengths enabled to calculate the diffuse double layer potentials and the corresponding surface charge in a DLVO framework. It was found that the so calculated surface charge densities were larger than those obtained by electrophoretic mobility measurements reported in a previous work. In addition it was found that surface charge densities grow with increasing volume fractions again in disagreement with the trend found via electrophoretic mobility measurements. The empirical postulation of an additional repulsion term enabled us to fit the experimental observation thus further showing the inadequacy of DLVO theory for highly charged polymeric latices such those studied here.

Once the foundations for the characterization of the colloidal stability of polymeric latices was laid and applied to model system, the problem of the size characterization of aggregating suspensions in flowing conditions was tackled. Due to its ability to deliver measurements online and in-situ, FBRM was chosen as size measurement technique. In order to properly interpret the measured signal, a mechanistic model for the corresponding particle detection was formulated thus obtaining the convolution relationship relating the measured CLD to the actual PSD. For the first time the exact expression for
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the characteristic weighting length appearing in such convolution relationship was given for any object of convex shape. This allowed the derivation of the relationships relating the moments of the CLD to the moments of the PSD. We then presented a thorough discussion of the effect of a variable shape on such relationships. This enabled the unequivocal definition of a size in terms of a FBRM measurement. Such definition was then applied to the case of the thin rod for which an analytical expression of the CLD was derived. It was shown how this experimental techniques, owing to its measuring principle, is not well suited for the monitoring of processes in which particulate systems grow mainly in one preferential direction. Based on these results it was then possible to successfully adopt such a sizing technique for the monitoring of the aggregation of a PVDC latex in a stirred vessel in fully destabilized conditions. Using very simple relationships the characteristic times of aggregation and micromixing were evaluated and compared for industrially relevant conditions (i.e. high solid volume fractions and small primary particle sizes). It was found that in these conditions latices aggregate and even gel before mixing is complete. Such conditions were then studied experimentally by feeding an electrostatically stabilized PVDC concentrated latex in a stirred vessel operated in semi batch mode together with a salt solution at concentrations above the CCC. Results showed a unequivocal interplay between mixing and aggregation/gelation as expected. The results were interpreted in terms of competition between aggregation/gelation and meso- and micromixing where, in the utilization of the available mixing models, care was taken to properly account the peculiarities of an aggregating system as opposed to standard chemical reactions. The general trend was that when gelation is faster than mixing at intermediate and small scales, the latex volumes gel before the surrounding turbulent flow can break them down to either the Kolmogorov in the case of mesomixing, or to scales small enough to allow for diffusion in the case of micromixing. The final size of the aggregates is then determined by the competition between the two processes. They tend to be larger the faster gelation can freeze in the latex volume and the slower mixing breaks them through the turbulent stretching and folding mechanism. This conclusion is supported by the scanning electron microscope images of the final aggregates. In the case of the fastest gelation times, i.e. at large feed solid volume fractions, they still exhibit a lamellar structure resembling the shape of the fluid folding during mixing at the outlet of the feed pipe. Due to the relative similarity between the micro- and mesomixing time most probably both mechanisms play a role on the experimental observations. However, considering the approximations involved in the estimation of the relevant characteristic times, these conclusions have to be regarded as qualitative.
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