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(Ultra-) Small angle X-ray scattering on asphaltenes: mathematical modelling and physical conclusions

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(Ultra-) Small Angle X-ray Scattering on asphaltenes:
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by
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Study performed at the department of Engineering Mathematics and Physics (ORTET/6) of the Shell Research and Technology Centre, Amsterdam

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Abstract

Scattering experiments are a common method in material analysis. Among them, X-ray diffraction is a method to study the structure of optical non-transparent media. The interference pattern of the diffracted X-rays, the spectrum, can be split in two parts, namely the Wide Angle X-ray Scattering (WAXS) and the Small Angle X-ray Scattering (SAXS). The (U)SAXS-spectrum is formed by the 0th order maximum of the interference pattern and it corresponds to structures with a length scale of about 1 nm to 2 nm. Thus, this method is very appropriate to examine large colloidal structures, like formed by asphaltenes, which are large flat molecules. These molecules are interesting since they cause pre-eminently pollution in oil processing (cokes-formation).

A SAXS-spectrum is hard to interpret since it is an interference pattern. This is especially true in case of complicated aggregates. Within Shell Research the computer program ParStruc is available to simulate diffraction spectra numerically. Complementary, we have derived a new analytical model, which includes both the primary particles and the aggregates. Here, concepts like polydispersion, fractal structure and orientation correlation of flat molecules will be under discussion.

Subsequently, this analytical model has been used, in combination with ParStruc, to interpret experimental SAXS data, as have been measured on several colloidal asphaltene mixtures with different thermodynamical stability.
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Preface

This thesis is part of a graduation project to obtain a master's degree in Applied Physics (Eindhoven University of Technology), performed from March 1996 until December 1996 at Shell Research and Technology Centre, Amsterdam (SRTCA) and supervised by Prof. Dr. M.A.J. Michels.

First of all my thanks go to Shell for giving me the opportunity to do this research at SRTCA and in particular M.A.J. Michels and P.A.J. Hilbers, working at the ORTET/6 department at SRTCA, for guiding me through. Many thanks also go to Ralph Haswell, Frans v.d. Berg, Henk Brandt and Roland Heijnis who have made the experimental data available. Finally, I also thank my fellow trainees for making my stay in Amsterdam a pleasant one.

Bart Markvoort
Chapter 1

Introduction

1.1 Asphaltenes

The petroleum industry is often called mature, however little is understood about the relationship between the structure and the properties of its basic material, petroleum. Crude oil is a complex colloidal system. In the refinery process 60–70% can be separated into easily refinable fractions by distillation. The residual material is called vacuum residue (VR). Such petroleum resids are complex mixtures of thousands of compounds of low volatility. It can be separated into pseudocomponents: coke, asphaltenes, resins, aromatics and saturates. The most common pseudocomponents are asphaltenes, which are defined as the part soluble in aromatic solvents (e.g. benzene or toluene) and insoluble in paraaffinic solvents (e.g. n-pentane or n-heptane).

Although asphaltenes form only a small percentage of crude oil, it is widely known that asphaltenes, which are the heaviest hydrocarbon molecules, are the most troublesome fractions for efficient processing in petroleum cracking and refining. They can precipitate under certain conditions in fuel tanks of sea-going ships and on the walls of refinery equipment.

The asphaltenes have not yet found their place in the official organic chemistry. They are in fact quite complex mixtures of substances with high and variable molecular masses (±1,000 – 10,000 u). However, according to their elementary composition, asphaltenes belong to a class of heteroatomic compounds, i.e. organic substances which contain, in addition to hydrogen and carbon, atoms such as oxygen, sulfur and nitrogen. The main structural characteristic of asphaltenes is the ‘hydrocarbon skeleton’ of their molecules which is made of three structural elements: (1) aromatic nuclei, (2) naphthenic nuclei and (3) side and bridged chains. A typical asphaltene molecule has been shown in figure 1.1.

One of the earliest and most significant studies on asphaltenes has been performed by Yen [1, 2]. According to this study, asphaltenes are condensed heterocyclic aromatic sheets with attached alkyl chains restricted to the plane of the sheet. These sheets have a diameter of 8.5–15 Å and are capable of associating in their third dimension in the presence of non-polar or slightly polar solvents to form stacked clusters about 16–20 Å in height. Such
clusters consist, depending on the asphaltene type and the environment it finds itself in, of about 5 sheets.

The association and clustering need not stop at the cluster (or particle) level. Molecular weight distribution studies have shown the presence of components of very large molecular weight. The particles are observed to associate to form micelles with diameters of the order of $100-300$ Å. This model is shown figure 1.2.

It is thus apparent that asphaltenes are not single, simple generic structures, but rather a complex mixture of colloidal entities (micelles of various sizes and shapes) consisting of assemblies of smaller particles, which in turn result from the clustering of lower-molecular-weight components, all in a state of solvents, temperature, pressure and fluid mechanical conditions.
Figure 1.2: Model of Yen: basic sheets form stacks which can agglomerate to yield large structures.
CHAPTER 1. INTRODUCTION

1.2 Small Angle X-ray Scattering

Scattering experiments are a common method in material analysis to gain information about the structure of crystals, molecules and atoms. The fundamental relation describing the diffraction of X-rays by crystalline matter, \( \lambda = 2d \sin \theta \), shows that the angle of diffraction varies inversely with the separation of the diffracting lattice planes. In ordinary crystals these lattice spacings are of the same order of magnitude as the X-ray wavelength (±1.54 Å), so the diffraction angles are rather large (Wide Angle X-ray Scattering). Colloidal dimensions (between tens and several thousand angstroms), however, are enormously large compared to X-ray wavelengths, which makes the observable scattering angles small (\( \leq 2\theta \)). So Small Angle X-ray Scattering is a technique for studying structural features of colloidal size.

Diffraction is produced by the interference of waves scattered by an object. In the case of X-rays striking the object, every electron becomes the source of a scattered wave. The scattered waves are coherent, though incoherent Compton scattering will occur too; this can be neglected as only small angles are involved. The scattered waves all have the same amplitude, but because of the path length difference, they have a different phase \( \phi \), which depends on the position of the electrons in space. These amplitudes are added and the intensity is then given by the absolute square of the resulting amplitude.

The calculation of the phase difference is illustrated in figure 1.3. Let us denote the direction of the incident beam by the unit vector \( \mathbf{s}_0 \) and the scattered beam by \( \mathbf{s} \). The path difference of two points, separated by \( \mathbf{r} \), is seen to be \( -\mathbf{r} \cdot (\mathbf{s} - \mathbf{s}_0) \). Since the phase \( \phi \) is \( \frac{2\pi}{\lambda} \) times the path difference and \( (\mathbf{s} - \mathbf{s}_0) \) is equal to \( 2\sin \theta \), the phase takes the form \( \phi = -q \cdot \mathbf{r} \), where \( q \) has the same direction as \( (\mathbf{s} - \mathbf{s}_0) \) and the magnitude: \( q = \frac{4\pi}{\lambda} \sin \theta \).

By introducing the concept of electron density \( \rho(\mathbf{r}) \), which is defined as the number of electrons per unit volume, and integrating over the whole space, the amplitudes of all secondary waves, represented by a term \( e^{-iqr} \)
each, can be added, to gain

\[ I(q) = F(q)F(q)^*; \quad F(q) = \int_V dr \rho(r) e^{-iq \cdot r}. \]  \hspace{1cm} (1.1)

So since the electrons are the primary scatterers, the scattering curve \( I(q) \) can be obtained from the electron density \( \rho(r) \) by Fourier transformation.

As mentioned above, the length scale that the scattering is describing, depends on the diffraction angle, namely according to: \( q \cdot r = 2\pi \). Here, we will discuss this, by example, for a configuration which we will meet again later. This configuration consists of widely separated compound spheres of diameter \( d \), built up themselves of discs with radius \( R \) that have random orientation.

For very small \( q \), \( qd \ll 1 \), the lengthscale we are looking at is very large compared to the diameter \( d \) of the compound spheres and the scattering will only be determined by the quantity of scatterers (figure 1.4a).

For \( qd \approx 1 \), we have zoomed in on the lengthscale of the spheres. The diffraction spectrum here (figure 1.4b) will be determined by the internal structure of the aggregates, and thus by the distribution of the discs which form the sphere.

When zooming in on smaller length scales (figure 1.4c), \( qR \approx 1 \), the information about the distribution is lost and the geometry of the discs is resolved.

When zooming in even further, the surface topology of the discs may be probed and the primary building particles, the atoms, may be determined (figure 1.4d).
1.3 This report

The target of this study is twofold. First, we want to develop an analytical model describing SAXS diffraction. Further, we want to determine the structure of different asphaltene mixtures with widely varying thermodynamical stability, combining our new analytical model and the computer program ParStruc (see appendix A).

In consequence, this report can be divided in two parts roughly. In the first part, which consists of the chapters 3–7, we will derive the analytical model. In order to do so, we will start with the diffraction spectrum of a single particle in chapter 3. However, in practice, we do not deal with single particles, but always the spectrum of a lot of particles at once is measured. The diffraction spectrum of such a system of particles will be determined by the primary particles as well as their mutual positions and orientations. In the chapters 4 and 5 we will derive the diffraction spectrum of such aggregates. However, when single particles aggregate, these particles are usually not distributed uniformly within the aggregates. But, depending on the aggregation mechanism a certain fractal structure may come into existence. Further, instead of only one, lots of aggregates will arise, all having a different size. The influence of these two features, fractal structure and polydisperse aggregates, is described in chapter 6. In chapter 7 we will conclude this part of the report with a survey of the model and we will enumerate which kind of structures yield which characteristics in a diffraction spectrum.

As a result, chapter 7 can also be seen as an introduction of the second part of this report, since it shows which characteristics of the spectrum can be used to determine the corresponding structure of the measured sample. The second part of this study is described in the chapters 8–10. In chapter 8 we will apply our model to some diffraction spectra found in the literature, in the following chapter to some in house (Shell) diffraction data on asphaltenes and finally in chapter 10 to some simulated diffraction spectra.

However, before we will start deriving our new analytical model, we will discuss in chapter 2 which work already has been performed in the area of SAXS diffraction on asphaltenes. Further, we will show here what the essential difference is between those studies and our approach.
Chapter 2

Earlier studies

Both SAXS and asphaltenes are not new topics. On both areas a lot of studies have been performed. In this chapter we will give a short review of the, for this study, most important work. For this purpose we will split the studies in two parts. The first about small angle X-ray scattering in general and the second about small angle X-ray scattering studies on asphaltenes.

2.1 SAXS in general

The principle of small angle X-ray scattering has already been outlined in the previous chapter. We saw that the diffraction spectrum could be written mathematically as

\[ I(q) = F(q)F^*(q) = \int dr \rho(r)e^{-iq\cdot r} \int dr' \rho(r')e^{iq\cdot r'}. \quad (2.1) \]

The first serious attempt to tackle this integral, by Debye [3], dates from 1915. The way of attack he used was to combine the two exponentials (step 1), thus looking to the distance between two scattering points, \( r'' \) (figure 2.1). The formula now shows

Figure 2.1: The method of Debye gives the diffraction spectrum using a distribution function of all distances \( r'' \) within the scatterers.
\[ I(q) = F(q)F^*(q) = \int dr \int dr' \rho(r)\rho(r')e^{-iq\cdot r''}, \quad (2.2) \]

where \( r'' = r - r' \). The next step Debye made was the assumption that the measured diffraction spectrum is the average over all possible orientations of the observed structure (step 2). Either because the structure would adopt all possible orientations in a certain period of time or because the total system consists of much of the same structures, all having their own orientation. The average over all orientations, all having equal probability, is mathematically equivalent to the average over all orientations of \( q \). For this averaging we will use the notation \(<\ldots>_{q} \). Because of this the exponential can be rewritten as
\[ <e^{-iq\cdot r''}>_{q} = \frac{\sin qr''}{qr''}. \quad (2.3) \]

Finally (step 3), the total diffraction spectrum can be written as
\[ <I(q)>_{q} = \int dr'' f(r'') \frac{\sin qr''}{qr''}, \quad (2.4) \]

where \( f(r'') \) is the distribution function of all distances within the structure. Thus, the problem is to find this distribution function, which can become very awkward for more complicated systems.

### 2.2 SAXS on asphaltenes

Since asphaltenes are such complex materials a multidisciplinary approach is necessary to be able to describe asphaltenes. A lot of research, both chemical and physical, has already been done on asphaltenes. It is beyond the context of this report to describe all these studies. The basic idea of asphaltenes, such as Yen’s model, has already been described in section 1.1. In this section we will describe some earlier work that has been performed in the area of SAXS diffraction on asphaltenes.

Three important groups that have been working and publishing on this topic, from about 1988, have to be mentioned, namely:

- **E. Y. Sheu et al.** Texaco,
- **S. H. Chen et al.** Exxon,
- **D. Espinat et al.** Institute Français du Petrole.

Characteristic of all their studies is that the mathematical analyses are based on the principle of Debye and that they only try to explain a small part of the total spectrum. Different aspects are treated in different studies. The first class of studies which is important deals with the influence of polydispersity of aggregate sizes, for example [9] of aggregates which sizes are distributed according to the Schultz distribution. The second important class deals with the internal structures of the aggregates, for example [10, 8, 14] fractal structures due to cluster aggregation are described. Further, it is worth
mentioning that especially Sheu sees the asphaltenes as large fractal aggregates, whereas Espinat talks about large 2-dimensional structures, namely discs that associate in a plane.

In the present study we have used some of the ideas of these studies and incorporated them in our model. But this work distinguishes itself essentially from the earlier studies by using a completely new approach. Whereas the former studies were all based on Debye, we will start over from the basic formula (1.1) and substitute a multipole expansion. The result will be a model which describes, distinct from the previous models, the whole spectrum and not only part of it. In the first instance the model has been derived for uniform aggregates built of discs. But, as we will see, it can be extended to contain almost all different aspects described above, yielding one model which can describe both single particles and aggregates, both uniform and fractal aggregates, and both mono- and polydispersed aggregates.
Chapter 3

A model for single particles

3.1 General formula

The most basic formula describing the X-ray diffraction spectrum of an object is:

\[ I(q) = F(q)F^*(q) = \int dr \rho(r)e^{-iq \cdot r} \int dr' \rho(r')e^{iq \cdot r'} \]  

(3.1)

In this chapter we will be concerned about the diffraction spectrum of a single particle. Figure 3.1 shows an arbitrarily shaped particle. It will be described by the electron density \( \rho(r) \), which will be taken unity within it and zero outside. Because there is only a single particle and \( \rho(r) \) is equal to zero outside, the integration volumes of both integrals, \( F(q) \) and \( F^*(q) \) are equal to the volume of this same particle.

There are different ways to solve these integrals for simple shapes. Mostly the average of the exponentials over \( \hat{q} \) is taken, which yields \( \sin(qr'')/(qr'') \). This method has been elaborated over half a century ago [4, 5, 6].

The average over \( \hat{q} \) was taken since the assumption had been made that in a real system all objects can have a random orientation relative to the incoming X-ray beam. In our way of approach we will make this same assumption, but yet at a later time. The essential point of our method is

Figure 3.1: The description of an arbitrarily shaped particle by means of a multipole expansion around its center of mass.

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that we will expand the exponentials in terms of spherical harmonics $Y_l^m$. We will do so by substituting the Rayleigh expansion,

$$e^{i\mathbf{q}\cdot\mathbf{r}} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i^l j_l(qr) Y_l^m(\hat{q}) Y_l^m(\hat{r}),$$  \hspace{1cm} (3.2)

resulting in

$$I(q) = (4\pi)^2 \sum_{l_1=0}^{\infty} \sum_{m_1=-l_1}^{l_1} \sum_{l_2=0}^{l_2} \sum_{m_2=-l_2}^{l_2} i^{l_1-l_2} Y_{l_1}^{m_1}(\hat{q}) Y_{l_2}^{m_2*}(\hat{q})$$  \hspace{1cm} (3.3)

This approach means that we will describe the scattering objects in terms of multipoles around their centers. It also has the advantage that it still holds for more complicated configurations, which we will meet later.

The case of single particles is of practical importance for dilute media. In this case, the particles scatter independently and the interparticle scattering is negligible because of the large average distance between them. Such a dilute medium will contain a lot of particles, each with its own orientation. Thus, the diffraction spectrum will be the average over all orientations. This is the same as taking the average over all directions $\mathbf{q}$ for only one particle. Because of the orthogonality of the spherical harmonics,

$$\frac{1}{4\pi} \int d\Omega Y_{l}^{m*}(\hat{q}) Y_{l'}^{m'}(\hat{q}) = \delta_{ll'} \delta_{mm'},$$  \hspace{1cm} (3.4)

the diffraction spectrum of a particle averaged over all orientations can be written as

$$< I(q) >_q = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \left| \int dr \rho(r) j_l(qr) Y_l^m(\hat{r}) \right|^2.$$

### 3.2 Sphere

#### 3.2.1 Analytical derivation

In case the scattering object contains some kind of symmetry, relation 3.5 will often simplify considerably. Because of the special spherical symmetry of a sphere, only the term with $l = m = 0$ will contribute to the spectrum. Because $Y_0^0 = \frac{1}{\sqrt{4\pi}}$, the integrand is independent of the direction $\hat{r}$, through which the volume integration is reduced to an integration over $r$,

$$< I(q) >_q = 4\pi \left| \int_0^R d\tau \tau^2 j_0(q\tau) Y_0^0(\hat{q}) \right|^2,$$

where $R$ is the radius of the sphere. This yields:

$$< I(q) >_q = \frac{(4\pi)^2}{q^2} \left| \int_0^R d(q\tau) (q\tau)^2 j_0(q\tau) \right|^2.$$

(3.7)
CHAPTER 3. A MODEL FOR SINGLE PARTICLES

Using two known relations for Bessel functions [11], namely:

\[ \frac{n+1}{z} j_n(z) + \frac{d}{dz} j_n(z) = j_{n-1}(z) \]  

(3.8)

and

\[ j_n(z) = \sqrt{\frac{\pi}{2z}} J_{\frac{1}{2} + \frac{n}{2}}(z), \]

relation 3.7 can be rewritten. This results in the following equation for the diffraction spectrum of a sphere.

\[ < I_{\text{sphere}}(q) > = \frac{9\pi V^2}{2} \left| \frac{J_{\frac{3}{2}}(qR)}{(qR)^{3/2}} \right|^2 \]

(3.9)

where \( V \) is the volume of the sphere. This result matches exactly the result of the other method mentioned before, e.g. [5].

3.2.2 Graphical representation and simulation

In the previous section, we have derived the diffraction spectrum of a sphere analytically. Another way to obtain diffraction spectra is by numerical computation (see appendix A). In this section we will compare the results (plots) of these two methods and in addition we will show the influence of some primary parameters on the spectrum.

The analytically derived spectrum is plotted in figure 3.2.a. for a sphere with a radius of unit length, where both x and y-axis have a logarithmic scale.

![Figure 3.2: Comparison of the diffraction spectra of a sphere with respectively radius 1 (A) and radius \(\frac{1}{2}\) (B).](image)

In this spectrum three regions can be regarded. For \( q < 1 \) we are looking at length scales very large compared to the radius of the sphere. Because of this the shape of the object cannot be noticed and the intensity only depends on the quantity of the diffracting mass. With \( \rho(r) = 1 \), the intensity is equal to the square of the volume of the sphere \( V^2 \). In the second region, \( q > 5 \), the intensity decreases according to \( q^{-4} \). Because of the double logarithmic
scale this yields a slope $-4$ in the spectrum, which is characteristic for a threedimensional, solid object. The third region mentioned is the transition between the previous two regions. The kink in the spectrum can, as expected, be found at $q \approx 3$, since the diameter $d$ of the sphere is equal to 2 and $qd \approx 2\pi$.

The primary parameter of a sphere is its radius $R$. The diffraction spectrum of a sphere with radius $\frac{1}{2}$ will have two major differences with that of a sphere with radius 1, which we have seen above. In the first place, the quantity of scattering mass has been decreased by a factor $2^3$. Because the intensity is related to the volume $V$ according to $V^2$, the intensity at small $q$ values, $qR \ll 1$, will be $\frac{1}{64}$ times the former. The second difference concerns the $q$ value of the kink. Because the length scale $L$ the diffraction is describing is related by $qL = 2\pi$, this kink will be shifted to the right, towards a higher $q$-value. These two differences are shown in figure 3.2.

Finally we will compare these analytical results with the result of the spectra derived numerically with PARSTRUC (Appendix A). Before we will compare the results, one essential difference between the two respective computation methods has to be outlined. Where the sphere has an uniform density distribution in the case of the analytical computation, in the case of numerical computation the object is built of points, in practice, the atoms. For example, in the numerical computation, the spectrum of the object, with radius 25 Å, plotted in figure 3.3 is computed.

![Figure 3.3: A 'sphere' built of 8144 C-atoms which has been used to calculate the diffraction spectrum of a sphere with ParStruc.](image)

This spectrum is shown in figure 3.4. It shows the same features as the analytically derived spectrum, shown in figure 3.2 up to $q \approx 2$ Å$^{-1}$. This corresponds with distances of about 3 Å. For larger $q$ values the internal structure of the sphere becomes important. In this case of nicely ordered C-atoms at center to center distance $l = 2$ Å, a peak appears at $q \approx 3$ Å$^{-1}$, as is to be expected since $ql = 2\pi$. 
3.3 Disc

3.3.1 Analytical derivation

The next object we will discuss is a disc. We will consider a disc as a very flat cylinder of radius $R$ and height $h$ (see figure 3.5). Also a disc shows a special symmetry. Again, we can make the most of this symmetry by applying spherical coordinates. Namely, in spherical coordinates, the integration over such a particle can be described by the height $h$ times the integration over the circle with radius $R$ given by $\theta = \frac{\pi}{2}$.

In deriving the diffraction spectrum we will again proceed from formula 3.5. The spherical harmonics $Y_{l}^{m}(\theta, \phi)$ can be expressed in terms of the associated Legendre functions according to:

$$Y_{l}^{m}(\theta, \phi) = (-1)^{m} \left[ \frac{2l + 1}{4\pi (l + m)!} \right]^{\frac{1}{2}} P_{l}^{m}(\cos \theta) e^{im\phi}$$  \hspace{1cm} (3.10)

Because of the geometry of the disc, $\theta$ equals $\frac{\pi}{2}$ and the integration over $\phi$ yields zero except for $m = 0$. Thus, the integral over $\Omega = \theta, \phi$ can be solved:

$$\int_{0}^{2\pi} d\phi Y_{l}^{m}(\theta = \frac{\pi}{2}, \phi) = \left[ 2\pi \sqrt{\frac{2l + 1}{4\pi}} P_{l}(0) \right] \delta_{m,0}, \text{with}$$

$$P_{l}(0) = \begin{cases} (-1)^{p} \frac{(2p)!}{2^{(p)!}} & \text{if } l = 2p \\ 0 & \text{if } l = 2p + 1 \end{cases}$$  \hspace{1cm} (3.11)

Using formula 3.11 when integrating formula 3.5 over the volume of the disc, the diffraction spectrum of a disc is given by

$$< I_{\text{disc}}(q) > q = \frac{4V^2}{(qR)^4} \sum_{l=0}^{\infty} \left[ \sqrt{4l + 1} \frac{(2l)!}{4l!(l)!^2} \int_{0}^{qR} d(qr) (qr) j_{2l}(qr) \right]^{2}$$  \hspace{1cm} (3.12)
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3.3.2 Graphical representation and simulation

In this section we will plot the analytically derived spectrum, just like we did for the sphere. We will compare it to the numerically derived one and study the influence of the primary parameters, its radius and its height.

In figure 3.6 the diffraction spectrum is plotted for a disc with radius $R = 10$ and volume $V = 1$ and for a disc with radius $R = 5$ and volume $V = \frac{1}{4}$.

The comparison with the diffraction spectrum of a sphere is striking in that sense that we can discern three regions again. In the first one, $q < R^{-1}$, the intensity is again depending on the volume of the disc. In the second one, $q > R^{-1}$, the intensity decreases according to $q^{-2}$, slope $-2$ on a log-log plot, characteristic for a flat object. And again the third region contains the transition.

Also the same differences as occurred for two spheres with different radii, can be seen here again, namely: decreasing intensity and a shift of the $q$-value of the kink towards larger values in case of decreasing the volume of the scatterer by reducing its radius. However, the volume of a disc decreases
only by a factor $2^2$ when the radius is halved. So the intensity will drop by a factor 16, instead of a factor 64.

The diffraction spectra of two discs have been computed numerically with ParStruc. The first disc is an 'infinitely' thin disc since it consists of only one layer of atoms. The second disc consists of five layers of atoms, because of which it has a finite thickness of 10 Å. The configuration of both discs is shown in figure 3.7. (The 'thick' disc in this figure has a radius of 50 Å, whereas the spectrum has been computed of a disc of radius 100 Å, but a plot of such a disc would yield one black plane where no separate atoms can be distinguished anymore.)
Figure 3.8: The diffraction spectra of the discs shown in figure 3.7 as calculated with ParStruc.

object.
Chapter 4

A model for compound particles

4.1 General theory

As mentioned before (section 1.1), Yen et al. have developed a model for asphaltenes in which the asphaltenes are built up as stacks of about 5-6 discs. So the next logical step in our derivations will be to describe the spectrum of such a stack of discs.

In the previous chapter we only studied the effect of one single particle. However, when there are two particles close together the total diffraction spectrum will be the sum of two contributions, namely one as a result of the separate particles and one as a result of their relative positions. The proof of this can be given by the basic scattering formula 3.1, which can also be written as:

\[ I(q) = \left| \int_V d\mathbf{r} \rho(\mathbf{r}) e^{-iq \cdot \mathbf{r}} \right|^2 \]

(4.1)

The configuration of two particles is shown in figure 4.1. The integration volume \( V \), the whole space, can be divided into three parts, namely the volume of particle one \( V_1 \), the volume of particle two \( V_2 \) and finally the remaining space. Integration over the latter volume however doesn't yield any contribution because in that part of the space holds \( \rho = 0 \).

The scattered intensity is, according to 4.1, given by the square of the integral. This yields:

\[ \left| \int_{V_1} d\mathbf{r} + \int_{V_2} d\mathbf{r} \right|^2 \rightarrow \left| \int_{V_1} d\mathbf{r} \right|^2 + \left| \int_{V_2} d\mathbf{r} \right|^2 + 2 \int_{V_1} d\mathbf{r} \int_{V_2} d\mathbf{r} \]

(4.2)

The first two contributions arise from respectively particle one and particle two, whereas the third arises from their mutual influence. The way to calculate the former two contributions has been explained in the previous chapter. Here, we will develop the last contribution and this gives us a perfect opportunity to show why we use spherical harmonics to derive the diffraction spectrum.
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Figure 4.1: The description of two particles by means of a multipole expansion around their respective centers of mass, which are \( R_{12} \) apart.

To start with, we will assume both particles to be identical and to have the same orientation, like shown in figure 4.1. The integral that has to be solved shows:

\[
h_2(q) = \int dr \rho(r) e^{-iq \cdot r} \int dr' \rho(r') e^{iq \cdot r'}.
\]

The two integration variables, \( r \) and \( r' \) both have the same origin \( O \), which is defined in the center of mass of particle one. However, we can also describe particle two with a new variable \( r_2 \) around its own center of mass \( O' \). Because both particles are identical, this yields two integrals with the same integration volume \( V_1 \). Since the relation between \( r' \) and \( r_2 \) is given by

\[
r' = R_{12} + r_2,
\]

formula 4.3 can be simplified to

\[
I_{12}(q) = \int_{V_1} dr e^{-iq \cdot r} \left| e^{iq \cdot R_{12}} \right|^2.
\]

Thus, the total diffraction spectrum of the two identical particles with the same orientation is:

\[
< I(q) > \hat{q} = \left< \left( 2 + 2e^{-iq R_{12}} \right) \left| \int_{V_1} dr e^{-iq \cdot r} \right|^2 \right> \hat{q}
\]

\[
= \left< \sum_{i=1}^{2} \sum_{j=1}^{2} \int_{V_1} dr e^{-iq \cdot r} \left| e^{iq R_{ij}} \right|^2 \right> \hat{q},
\]

since \( R_{11} = R_{22} = 0 \). In the following section we will elaborate this general equation for the special configuration of a stack of discs.

4.2 Stack of disks

A stack of discs is an excellent example of identically shaped particles, all with the same orientation. However, a stack is built of \( N \) instead of 2
particles. In order to derive the diffraction spectrum of such a stack, we will again start from formula 3.1. Further, we will again use the special geometry of the stack, namely $N$ discs, all having the same orientation $\mathbf{n}$, which is again parallel to the vector, $\mathbf{R}_{ij}$, connecting the centers of mass of the discs. (See figure 4.2.)

The stack is built of $N$ discs. This means that every pair of discs $(i, j)$ will give a contribution to the total spectrum like described in the previous section. Therefore, we will first derive this contribution of one pair of discs. To derive this contribution we will first substitute the Rayleigh expansion in formula 4.5, yielding:

$$I_{ij}(\mathbf{q}, \mathbf{R}_{ij}) = \int_{V(\mathbf{n})} d\mathbf{r}_i \int_{V(\mathbf{n})} d\mathbf{r}_j \sum_{l_1,m_1} \sum_{l_2,m_2} \sum_{L,M} \left(4\pi\right)^{3-l_1+l_2+L}(-1)^{m_1+m_2+M} j_{l_1}(qr_i) j_{l_2}(qr_j) j_L(q\mathbf{R}_{ij})$$

$$\times \left[ Y_{l_1}^{-m_1}(\hat{r}_i) Y_{l_2}^{m_2}(\hat{r}_j) Y_{L}^{M}(\hat{R}_{ij}) Y_{l_1}^{m_1}(\hat{q}) Y_{l_2}^{-m_2}(\hat{q}) Y_{L}^{-M}(\hat{q}) \right].$$

The summation over all spherical harmonics $Y_{L}^{M}(\hat{R}_{ij})$, resulting from the relative position of the respective discs, can be simplified because of the special configuration. Because $\mathbf{R}_{12}$ is parallel to the $z$-axis, $\theta = 0$. Substituting this in equation 3.10 gives that $M = 0$, since

$$P_{L}^{M}(1) = \begin{cases} 1 & \text{if } M = 0 \\ 0 & \text{if } M \neq 0. \end{cases}$$

Further, we will introduce the generalised Gaunt coefficient [16], which is defined as

$$\left\langle \begin{array}{ccc} l_1 & \ldots & l_n \\ m_1 & \ldots & m_n \end{array} \right\rangle = \frac{1}{4\pi} \int d\Omega \prod_{i=1}^{n} \left[ \frac{4\pi}{2l_i + 1} \right]^{\frac{1}{2}} Y_{l_i}^{m_i}(\Omega).$$

Figure 4.2: Graphical representation of the configuration of a stack.
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For further definitions of 3j-symbols and rotation operators which we will meet later, we would like to refer to Messiah [17]. Substituting the Gaunt coefficient and $M = 0$ yields

\[
< I_{ij}(q, R_{ij}) > = \int_{V(n)} \int_{V(n)} \sum_{l_1, m_1, l_2, m_2} \sum_{L} 4\pi i^{-l_1+l_2+L} \times (-1)^{m_1+m_2} [(2l_1 + 1)(2l_2 + 1)(2L + 1)]^{1/2} \times j_{l_1}(qr_i) j_{l_2}(qr_j) j_{L}(qR_{ij}) Y_{l_1}^{m_1} (\hat{r}_i) Y_{l_2}^{m_2} (\hat{r}_j) \times (2L + 1)^{1/2} \left[ \begin{array}{ccc} l_1 & l_2 & L \\ m_1 & -m_2 & 0 \end{array} \right],
\]

(4.10)

for the contribution to the diffraction spectrum of one pair of discs $(i, j)$. Here $i$ may be equal to $j$. Since $R_{ii} = 0$, this describes the contribution of the separate discs (intraparticle), whereas the terms with $i \neq j$ describe the interparticle scattering.

The next property of the stack we assume, is that all discs have the same orientation. Their normal vectors have been chosen parallel to the $z$-axis. This gives $m_1 = 0$ and $m_2 = 0$ because, like in section 3.3, integration of a spherical harmonic $Y_l^m(\Omega)$ over the volume of a disc, with normal vector parallel to the $z$-axis, is zero except for $m = 0$. So we can apply formula 3.11 again, yielding the result

\[
< I_{ij}(q, R_{ij}) > = \sum_{l_1, l_2} i^L (4l_1 + 1)(4l_2 + 1)(2L + 1) \times \left[ 2\pi h \int d(qr_i) (qr_i) j_{2l_1}(qr_i) \right] \times \left[ 2\pi h \int d(qr_j) (qr_j) j_{2l_2}(qr_j) \right] \times \frac{(2l_1)!}{4^{l_1}(l_1)!^2} \frac{(2l_2)!}{4^{l_2}(l_2)!^2} \left[ \begin{array}{ccc} 2l_1 & 2l_2 & L \\ 0 & 0 & 0 \end{array} \right] j_L(qR_{12}).
\]

(4.11)

The Gaunt symbol in formula 4.11 can be written as the product of two 3j-symbols [17]. In this particular case, where $m_1 = m_2 = M = 0$, it is even the square of a 3j-symbol

\[
\left[ \begin{array}{ccc} a & b & c \\ 0 & 0 & 0 \end{array} \right] = \left[ \begin{array}{ccc} a & b & c \\ 0 & 0 & 0 \end{array} \right]^2.
\]

(4.12)

This particular 3j-symbol, where the second row contains only zeros, is zero when the sum of the elements in the first row, $a + b + c$, is odd. However, when this sum is even:

\[
\left( \begin{array}{ccc} a & b & c \\ 0 & 0 & 0 \end{array} \right) = (-1)^p \frac{(-a + b + c)!(a - b + c)!(a + b - c)!}{(a + b + c + 1)!} \times \frac{p!}{(p - a)!(p - b)!(p - c)!},
\]

(4.13)
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where \( a+b+c=2p \).

Because the 3j-symbol is zero for odd \( a+b+c \), the contribution to \( \langle I_{ij}(q, \mathbf{R}_{ij}) \rangle_q \) is zero for odd \( L \). Using this and relation 4.13, equation 4.11 can be rewritten as

\[
\langle I_{ij}(q, \mathbf{R}_{ij}) \rangle_q = \frac{4V^2}{(qR)^4} \sum_{l_1, l_2} (-1)^l \left[ \prod_{p=1}^{2} \left( \int_{0}^{qR} dx x^2 j_{2l_p}(x) \right) \right] \times (4l_1+1)(4l_2+1)(4L+1) \frac{(2l_1)!}{4^{l_1}(l_1)!^2} \frac{(2l_2)!}{4^{l_2}(l_2)!^2} \times \frac{(l_1 + l_2 + L)!}{((-l_1 + l_2 + L)!(l_1 - l_2 + L)!(l_1 + l_2 - L)!)}^2 \times \frac{(-2l_1 + 2l_2 + 2L)!(2l_1 - 2l_2 + 2L)!(2l_1 + 2l_2 - 2L)!}{(2l_1 + 2l_2 + 2L + 1)!} \times j_L(qR_{12}).
\]

The total diffraction spectrum of a stack of \( N \) discs is given by the sum of the contributions of all possible pair combinations \((i, j)\)

\[
\langle I_{\text{stack}}(q) \rangle_q = \sum_{i=1}^{N} \sum_{j=1}^{N} \langle I_{ij}(q, \mathbf{R}_{ij}) \rangle_q \quad (4.15)
\]

\[
= N \langle I_{\text{disc}}(q) \rangle_q + 2 \sum_{i=1}^{N} \sum_{j=i+1}^{N} \langle I_{ij}(q, \mathbf{R}_{ij}) \rangle_q,
\]

where \( \langle I_{\text{disc}}(q) \rangle_q \) is given by equation 3.13 and \( \langle I_{ij}(q, \mathbf{R}_{ij}) \rangle_q \) by equation 4.14.

In the special case that all vectors \( \mathbf{R}_{ij+1} \) for two successive discs are equal, with magnitude \( \Delta z \), relation 4.15 can be simplified

\[
\langle I_{\text{stack}}(q) \rangle_q = N \langle I_{\text{disc}}(q) \rangle_q + 2 \sum_{t=1}^{N-1} (N - t) \langle I_{12}(q, t\Delta z) \rangle_q, \quad (4.16)
\]

where \( \langle I_{12}(q, t\Delta z) \rangle_q \) is the contribution of two discs in the stack at a relative position of \( t \) times the interdisc distance.
Chapter 5

Aggregates of anisotropic particles

5.1 General theory

In the previous chapter we have looked at the diffraction spectrum of nicely ordered particles, all having the same orientation and a 100% correlation between this orientation and their relative positions. In this chapter, we will treat another kind of configuration we are interested in. Namely, \( N \) particles, all having their own orientation, positioned within a certain volume. An example is shown in figure 5.1. We will call this configuration an aggregate.

![Figure 5.1: The configuration of an aggregate of randomly positioned particles.](image)

The total diffraction spectrum will once again be determined by the sum of the contributions of all possible pair combinations:

\[
I(q) = \sum_{l=1}^{N} \sum_{m=1}^{N} \int_{V(n_l)} dr_l e^{-iq \cdot r_l} \int_{V(n_m)} dr_m e^{iq \cdot r_m} e^{-iQ \cdot R_{lm}},
\]

(5.1)

where \( R_{lm} \) is the center to center distance of the two respective discs and the integrations are over a volume determined by the respective orientations of the particles \( n_l \). However, the two particles do not necessarily have the same orientation and their orientation and their relative position are not
Figure 5.2: The description of two randomly oriented particles by means of a multipole expansion around their respective centers of mass, which are $R_{im}$ apart.

necessarily correlated. An example of such a pair combination is shown in figure 5.2.

Because the diffraction spectrum depends only on the distances in the distribution of the scatterers, we can take the average over all possible orientations, $n_l$ and $n_m$ of the particles and all possible directions $R_{lm}$. In this way, the position and orientation of the $N$ particles can be described by a distribution function $f(n_l, n_m, R_{lm})$, which is chosen to be normalized to unity. The spectrum can be separated into two parts. The first part is the contribution of the separate particles, $l = m$, and the second part describes the contribution of the interference between different particles, $l \neq m$.

\[
I(q) = N \int \int_{V(n)} \left| \int_{V(n)} dr e^{-iqr} \right|^2 
+ N(N-1) \int_{V} dR_{12} \int \int_{\Omega} d\Omega \int_{V(n_1)} \int_{V(n_2)} dr_1 dr_2 e^{-i(qr_1 + qr_2 + qR_{12})} f(n_1, n_m, R_{lm}).
\]

The former contribution to the diffraction spectrum has already been treated in chapter 3. In the latter part we may again substitute the Rayleigh expansion and a Gaunt coefficient. This results in

\[
< I(q) > \hat{q} = N \left| \int_{V(n)} dr e^{-iqr} \right|^2 
+ N(N-1) \int_{V} dR_{12} \int \int_{\Omega} d\Omega \int_{V(n_1)} \int_{V(n_2)} dr_1 dr_2 \sum_{l_1, m_1, l_2, m_2} \sum_{L, M} i^{-l_1+l_2+L} (-1)^{m_1+m_2+M} \left\{ \frac{(2l_1 + 1) (2l_2 + 1)}{4\pi} \frac{(2L + 1)}{4\pi} \right\}^{1/2} 
\]
\[
\times (4\pi)^3 \left\{ \frac{l_1}{m_1} \frac{l_2}{-m_2} \frac{L}{-M} \right\} j_{l_1}(q_{r_1}) j_{l_2}(q_{r_2}) j_L(q_{R_{12}}) 
\times Y_{l_1}^{-m_1}(\hat{r}_{1}) Y_{l_2}^{-m_2}(\hat{r}_{2}) Y_{L}^{M}(\hat{R}_{12}) f(n_1, n_2, R_{12}).
\]
5.2 An aggregate of discs

In this section, we will elaborate the general theory for the case of a system of discs in which the chance of finding two discs at a distance $R_{12}$ from each other is independent on the direction of $R_{12}$. This is illustrated in figure 5.3, where both configurations are equally probable since the distance between the centers of mass of the two discs is equal in both cases. This assumption has been made out of mathematical point of view, since it yields some essential mathematical advantages. However, physically it is not completely correct. In fact, two discs close together will force each other in a certain direction.

However, we have to make this assumption, because it has two consequences which simplify our problem considerably:

- $L = 0$ because $R_{12}$ is independent on the direction of $R_{12}$.
- Because the distribution function has to be a scalar, it can only depend on the inner product of the orientations of the discs: $f(n_1 \cdot n_2, R_{12})$.

Because $L = 0$ the Gaunt coefficient can be written as:

$$
\left\langle \frac{l_1}{m_1} \frac{l_2}{m_2} \right\rangle = \frac{(-1)^{m_1}}{2l_1 + 1} \delta_{l_1, l_2} \delta_{m_1, m_2}
$$

(5.4)

and $Y_L^M(\Omega) = Y_0^0(\Omega) = \sqrt{\frac{1}{4\pi}}$. So relation 5.3 may be written as

$$
<I(q)_q = N \frac{2V^2}{(qR)^2} \left(1 - \frac{1}{qR} J_1(2qR)\right)
$$

(5.5)

$$
+ \int_V dR_{12} \int_\Omega d\mathbf{n}_1 \int_\Omega d\mathbf{n}_2 \int_{V(n_1)} dr_1 \int_{V(n_2)} dr_2
$$

$$
\times N(N - 1)(4\pi)^{3/2} \sum_{l,m} j_l(qr_1) j_l(qr_2) j_0(qR_{12})
$$

$$
\times Y_l^m(\hat{\mathbf{r}}_1) Y_l^m(\hat{\mathbf{r}}_2) Y_0^0(\hat{R}_{12}) f(\mathbf{n}_1 \cdot \mathbf{n}_2, R_{12}).
$$

Because of the relative orientation of the two discs, their normal vectors include a certain angle $\beta$. Thus, the two discs will be described in another
set of spherical harmonics. However, the spherical harmonics describing the latter can be rotated to coincide the former, using the rotation operator $R_{lm'}^{m''}$ [17]

$$\sum_{l_2m_2} Y_{l_2}^{m_2}(\Omega_2) = \sum_{l_2m_2} \sum_{m'} R_{l_2}^{m_2m'} Y_{l_2}^{m'}(\omega_2). \quad (5.6)$$

The integration over $\phi$ is, for the same reasons as we have seen before in section 3.3, unequal to zero only in case $m_1 = m' = 0$. According to equation 5.4 $m_1 = m_2$, so all summations over $m$ will disappear, resulting in

$$< I(q) >_q = \frac{N 2V^2}{(qR)^2} \left( 1 - \frac{1}{qR} J_1(2qR) \right) \quad (5.7)$$

$$+ \frac{N(N - 1) \int dR_{12} \int d\Omega_1 \int d\Omega_2 \sum_{l=0}^{\infty} 4\pi}{2V^2 (qR)^4} \times \int_{V(n_1)} d\Omega_1 Y_0^{0}(\hat{r}_1) j_l(qr_1) \int_{V(n_2)} d\Omega_2 R_{l}^{00} Y_0^{0}(\hat{r}_2) j_l(qr_2) \times j_0(qR_{12}) f(n_1 \cdot n_2, R_{12}). \quad (5.8)$$

The rotation operator $R_{l}^{00} = P_l(\cos \beta)$ is independent of $r_2$, so it can be put outside the integral over $r_2$:

$$< I(q) >_q = \frac{N 2V^2}{(qR)^2} \left( 1 - \frac{1}{qR} J_1(2qR) \right) \quad (5.9)$$

At this point in the derivation we have to have a closer look at the distribution function. Till now, we have assumed that the chance of finding two discs at a distance $R_{12}$ from each other is independent on the direction of $\Omega_{12}$. Because of this assumption, the distribution function $f(n_1 \cdot n_2, R_{12})$ could be written as $f(n_1 \cdot n_2, R_{12})$, only depending on the absolute distance between the discs and the angle between their normal vectors. This distribution function can be expanded in a complete orthonormal set of Legendre functions

$$f(n_1 \cdot n_2, R_{12}) = \sum_{k=0}^{\infty} c_k f_k(R_{12}) P_k(n_1 \cdot n_2). \quad (5.9)$$

Because of the symmetry of a disc, $n_1$ and $-n_1$ will result in the same disc. Because of this we are looking for an even function, so the terms with odd $k$ will be zero. We want to normalize the distribution function to unity. But integrating over the whole space and all orientations will only normalize $f_0$,.
because the integration of \( P_{2k}(\cos \theta) \) is zero except for \( k = 0 \).

\[
\int_V dR_{12} \int_\Omega d\mathbf{n}_1 \int_\Omega d\mathbf{n}_2 f(\mathbf{n}_1 \cdot \mathbf{n}_2, R_{12}) = \int_V dR_{12} \int_\Omega d\mathbf{n}_1 \int_\Omega d\mathbf{n}_2 \frac{1}{(4\pi)^2} f_0(R_{12}) = 1. \tag{5.10}
\]

The other functions \( f_{2k} \) can be determined in another way. The expectation value of \( P_{2k}(\mathbf{n}_1 \cdot \mathbf{n}_2) \) is defined as

\[
\langle P_{2k}(\mathbf{n}_1 \cdot \mathbf{n}_2) \rangle = \frac{\int dR_{12} \int_\Omega d\mathbf{n}_1 \int_\Omega d\mathbf{n}_2 f(\mathbf{n}_1 \cdot \mathbf{n}_2, R_{12}) P_{2k}(\mathbf{n}_1 \cdot \mathbf{n}_2)}{\int dR_{12} \int_\Omega d\mathbf{n}_1 \int_\Omega d\mathbf{n}_2 f(\mathbf{n}_1 \cdot \mathbf{n}_2, R_{12})}. \tag{5.11}
\]

With this equation, the coefficients \( c_{2l} \) can be determined by normalizing the integral of \( f_{2l}(R_{12}) \) over \( \mathbf{R}_{12} \) to unity. Thus, the distribution function becomes

\[
f(\mathbf{n}_1 \cdot \mathbf{n}_2, R_{12}) = \sum_{k=0}^{\infty} \frac{\langle P_{2k}(\mathbf{n}_1 \cdot \mathbf{n}_2) \rangle}{\langle P_{2k}(\mathbf{n}_1 \cdot \mathbf{n}_2) \rangle^2} f_{2k}(R_{12}) P_{2k}(\mathbf{n}_1 \cdot \mathbf{n}_2). \tag{5.12}
\]

Substituting this result for the distribution function into formula 5.8 gives

\[
\langle I(\mathbf{q}) \rangle_q = N \frac{2V^2}{(qR)^2} \left( 1 - \frac{1}{qR} J_1(2qR) \right) + N(N-1) \int_V dR_{12} \int_\Omega d\mathbf{n}_1 \int_\Omega d\mathbf{n}_2 \times \left( \sum_{l=0}^{\infty} \sum_{k=0}^{\infty} 4V^2 \left| \frac{\sqrt{4l+1} - \frac{(2l)!}{4^l(l!)^2} \int_0^{qR} \int_0^{(2l)!} d(qr) J_l(qr) j_{2l}(qr) \right|^2 \right.
\]

\[
\left. \times \frac{\langle P_{2k}(\mathbf{n}_1 \cdot \mathbf{n}_2) \rangle}{\langle P_{2k}(\mathbf{n}_1 \cdot \mathbf{n}_2) \rangle^2} \sum_{l=0}^{\infty} \sum_{k=0}^{\infty} 4V^2 \left| \frac{\sqrt{4l+1} - \frac{(2l)!}{4^l(l!)^2} \int_0^{qR} \int_0^{(2l)!} d(qr) J_l(qr) j_{2l}(qr) \right|^2 \times \frac{\langle P_{2k}(\mathbf{n}_1 \cdot \mathbf{n}_2) \rangle}{\langle P_{2k}(\mathbf{n}_1 \cdot \mathbf{n}_2) \rangle^2} \sum_{l=0}^{\infty} \sum_{k=0}^{\infty} 4V^2 \left| \frac{\sqrt{4l+1} - \frac{(2l)!}{4^l(l!)^2} \int_0^{qR} \int_0^{(2l)!} d(qr) J_l(qr) j_{2l}(qr) \right|^2 \times \int_V dR_{12} j_0(qR_{12}) f_{2l}(R_{12}), \tag{5.13}
\]

in which \( \langle P_{2l}(\mathbf{n}_1 \cdot \mathbf{n}_2) \rangle \) is called an order parameter, which can have any value between zero, in the limiting case that all orientations are random, and one, when all normal vectors have the same orientation.
5.2.1 Limiting cases

There are two limiting cases in the orientations of the discs. On the one hand all discs may have a random orientation and on the other hand all discs may be parallel. These two cases are schematically shown in figure 5.4. Each point in this figure should then be replaced by a disc, with its normal in the direction of the arrows.

![Schematic view of two possible configurations: random orientation (a) parallel orientation (b).](image)

When all discs have random orientations, $< P_{2l}(n_1 \cdot n_2) >$ is equal to zero for $l \neq 0$. This means that all terms with $l \neq 0$ will be equal to zero, resulting in the diffraction spectrum:

$$< I(q) >_{\hat{q}} = N \frac{2V^2}{(qR)^2} \left( 1 - \frac{1}{qR} J_1(2qR) \right)$$

$$+ N(N-1) \frac{4V^2}{(qR)^4} \left| 1 - \cos(qR) \right|^2$$

$$\times \int_V dR_{12} j_0(qR_{12}) f_0(R_{12}),$$

(5.15)

However, when all discs have the same orientation, $< P_{2l}(n_1 \cdot n_2) >= 1$, for every $l$, because the inner product of any two normal vectors is equal to one. Because all discs have the same orientation, all functions $f_{2l}(R_{12})$ are identical. So the diffraction spectrum can be written as:

$$< I(q) >_{\hat{q}} = N \frac{2V^2}{(qR)^2} \left( 1 - \frac{1}{qR} J_1(2qR) \right)$$

$$+ N(N-1) \frac{2V^2}{(qR)^2} \left( 1 - \frac{1}{qR} J_1(2qR) \right)$$

$$\times \int_V dR_{12} j_0(qR_{12}) f_0(R_{12}),$$

(5.16)

These two distributions mentioned above are two limiting cases of a more general distribution function, where the interaction between the discs results in an parallel orientation at short distances, but where this interacting force isn’t strong enough to give all discs the same orientation. So at a longer scale,
the discs will still have a random orientation. This model can be written by means of a descending exponential in the terms of the distribution function describing the orientation

$$f_{2l}(R_{12}) \rightarrow f_{2l}(R_{12})e^{-R_{12}/x}, \quad (5.17)$$

for $l \neq 0$. This gives the result

$$< I(q) >_q = N \frac{2V^2}{(qR)^2} \left( 1 - \frac{1}{qR} J_1(2qR) \right)$$

+ $N(N-1) \frac{2V^2}{(qR)^2} \left( 1 - \frac{1}{qR} J_1(2qR) \right) \int_V dR_{12} j_0(qR_{12}) f_{2l}(R_{12}) e^{-R_{12}/x}$

+ $N(N-1) \frac{4V^2}{(qR)^4} |1 - \cos(qR)|^2 \int_V dR_{12} j_0(qR_{12}) f_{2l}(R_{12}) \left( 1 - e^{-R_{12}/x} \right). \quad (5.18)$

### 5.2.2 Spherical system of discs

In order to derive the diffraction spectrum of a system of discs an assumption about the distribution of the discs has been made. This assumption is: the chance of finding two discs at a distance $R_{12}$ from each other is independent on the direction of $R_{12}$. Because of this the distribution function $f(n_1, n_2, R_{12})$ could be written as $f(n_1 \cdot n_2, R_{12})$.

Here we will make a second assumption about the distribution function. This assumption is that the discs are distributed uniformly within a sphere, where the correlation in orientation can be set by means of the order parameter $< P_{2l}(n_1 \cdot n_2) >$. The discs are randomly positioned within a sphere with radius $d$, so $f_0(R_{12})$ is the distribution function of distances occurring in a sphere [4]:

$$f_0(x) = 12x^2(1 - x)^2(2 + x), \quad (5.19)$$

where $x = \frac{R_{12}}{2d}$. With this distribution function, the integral becomes

$$\int_V dR_{12} j_0(qR_{12}) f_0(R_{12}) = \left( \frac{3\sin(qd) - qd\cos(qd)}{(qd)^3} \right)^2, \quad (5.20)$$

where $d$ is the radius of the spherical aggregate. The total diffraction spectrum of a spherical system of discs thus becomes

$$< I(q) >_q = N \frac{2V^2}{(qR)^2} \left( 1 - \frac{1}{qR} J_1(2qR) \right)$$

+ $N(N-1) \sum_{l=0}^{\infty} \frac{4V^2}{(qR)^4} < P_{2l}(n_1 \cdot n_2) >$

× $\left| \sqrt{4l + 1} \frac{(2l)!}{4^l(l!)^2} \int_0^{qR} d(qr) (qr) j_{2l}(qr) \right|^2$

× $\left( \frac{3\sin(qd) - qd\cos(qd)}{(qd)^3} \right)^2. \quad (5.21)$
5.3 Graphical representation and simulation

In this section we will compare the analytically derived spectrum of a spherical system of discs with those obtained numerically with PARSTRUC. We will pay special attention to the influence of the degree of order in the orientation and further, we will study the influence of the density of the system.

To start with, we will assume all discs to be randomly orientated. A schematic view of such configuration can be seen in figure 5.4a. Only a couple of points have been plotted here, however in the calculations we will use much more discs. Because all discs have a random orientation, \( < P_{2l}(n_1 \cdot n_2) > \) is equal to zero for \( l \neq 0 \). The total diffraction spectrum for this case is:

\[
< I(q) > = N \frac{2V^2}{(qR)^2} \left( 1 - \frac{1}{qR} J_1(2qR) \right)
+ N(N-1) \frac{4V^2}{(qR)^4} |1 - \cos(qR)|^2
\times \left( \frac{3\sin(qd) - qd \cos(qd)}{(qd)^3} \right)^2.
\]

From this equation, it is clear that there are two contributions to the diffraction spectrum. In the first place, there is a term which describes the contribution of the individual discs. This term increases linearly with the number of discs. The second term describes the interparticle scattering. This term increases quadratically with the number of discs. Both terms are plotted separately in figure 5.5, for the typical case of \( 10^6 \) discs with radius 1 within a sphere of radius 100. In this figure, the solid line shows the interparticle contribution and the dashed line the contribution of the separate discs.

![Figure 5.5: The two contributions to the diffraction spectrum of a spherical aggregate of discs, respectively resulting from the interparticle and the intraparticle scattering.](image)

Addition of these two contribution yields the total diffraction spectrum, which is shown in figure 5.6. It is clear that the total diffraction spectrum
is determined by the interparticle scattering for \( q < 0.5 \), whereas for \( q > 0.5 \) it is determined by the diffraction of the discs separately.

![Figure 5.6: The total diffraction spectrum of the aggregate of randomly oriented discs.](image)

In the diffraction spectrum shown in figure 5.6, three 'kinks' appear. Two of these have already been explained in the previous sections. The first, \( q \approx 0.03 \), is determined by the diameter of the spherical aggregate, whereas the second, \( q \approx 3 \), is determined by the diameter of the discs. The third kink is caused by the transition from the second to the first term in equation 5.22. The \( q \)-value this will occur for is determined by

\[
9(N - 1) = (qd)^4. \tag{5.23}
\]

In our example, \( N = 10^6 \) and \( d = 100 \), this gives \( q \approx 0.55 \). However, for a lower concentration, less discs within the same spherical volume, this kink would move towards a lower \( q \)-value, while the other kinks remain at their positions. As a result, the flat part in the spectrum would become wider.

The other limit is the case in which all discs have the same orientation. In that case, shown in figure 5.4b, \( < P_2(\mathbf{n}_1 \cdot \mathbf{n}_2) > \) is equal to 1, for all possible values of \( l \). In this case, where all discs have the same orientation, \( f_{2l}(x) = f_0(x) \) for all \( l \). Because of this, the integral over the volume of the sphere can be taken outside the summation, and the summation that rests is identical to the summation we have seen in the case of a single disc. This yields the following formula for the diffraction spectrum.

\[
< I(q) >_\parallel = N \frac{2V^2}{(qR)^2} \left( 1 - \frac{1}{qR} J_1(2qR) \right) \tag{5.24}
\]

\[
+ N(N - 1) \frac{2V^2}{(qR)^2} \left( 1 - \frac{J_1(2qR)}{qR} \right)
\]

\[
\times \left( \frac{3 \sin(qd) - qd \cos(qd)}{(qd)^3} \right)^{2}
\]

The difference between this formula, for parallel discs, and formula 5.22, for randomly oriented discs, is the factor \( \frac{2V^2}{(qR)^2} \left( 1 - \frac{J_1(2qR)}{qR} \right) \) instead of \( \frac{4V^2}{(qR)^4} \left[ 1 - \cos(qR) \right]^2 \). These two factors are plotted both in figure 5.7.
Figure 5.7: The two different factors, respectively in case of randomly oriented and parallel oriented discs, differ only for $q > 2$, where the aggregate contribution is already dominated by the contribution of the single particles.

In this figure can be seen that these two factors are equal up to $q R \approx 2$. The only difference between the two spectra is to be expected for $q > 2$. However, if we look at figure 5.5, it is clear that for $q > 2$ the diffraction spectrum is determined by the other term, the term describing the diffraction of the separate discs, while the contribution of the term describing the interparticle scattering, the term where the difference occurs, is at most one percent. The conclusion is that the diffraction spectra look identical whether the discs are randomly oriented or parallel to each other.

This result has also been verified numerically with PARSTRUC for the spectra of a system containing 100 discs with radius 10 randomly positioned within a sphere with radius 90. The spectra were computed once for all discs randomly oriented and once for all discs parallel, while the centers of mass of the discs were identical in both cases. These spectra are shown in figure 5.8.

We conclude that the diffraction spectra look identical whether the discs are randomly orientated or parallel to each other. But we have to be careful with this conclusion. It was drawn in case of $10^6$ discs with radius 1 within a sphere with radius 100, in which case every disc has an average space of the order of magnitude of a sphere with the same radius as the disc. However if we put more of those same discs within the same spherical space, the term in formula 5.22 describing the interparticle contribution to the scattering spectrum will get more influence, since this term increases quadratically with the number of discs, where the other term increases only linearly. This can also be seen from equation 5.23. As our reference point, we will use the example used before, namely $N_0 = 10^6$ discs with radius 1 within a sphere with radius $d_0 = 100$. If we increase the number of discs $N$ while keeping the radius of the aggregate constant, $q^4 \frac{N_0}{N} = C$, where $C$ is a constant. This shows a shift of the kink to higher $q$-values for a more dense packing of the discs. However, to obtain a different spectrum in the respective cases of randomly oriented and parallel discs, the $q$-value of the kink should be
about 2. This corresponds to a least $10^8$ discs, but $10^8$ discs of radius 1 within a sphere with radius 100 would yield a solid sphere, where no discs are visible anymore.

The second way to increase the $q$-value of the kink is decreasing the radius $d$ of the aggregate, while keeping the number of discs within a unit volume constant. In that case the number of particles decreases with $d^3$, resulting in the relation, $q^4 \frac{d}{d_0} = C$, where $C$ is a constant. However, to obtain a difference between the two spectra, the diameter of the aggregate should be so small that it is impossible to speak about a sphere anymore.

The conclusion is that the diffraction spectrum of a sphere built of discs looks the same whether there is a strong correlation in the orientation of the respective discs or not. So, for such a configuration, it is impossible to tell something about the orientation correlation by scattering experiments.
Chapter 6

Polydisperse and fractal systems

6.1 Polydisperse aggregates

In chapter 3 we focussed on the diffraction spectrum of a single particle. In chapter 4 we zoomed out to derive the spectrum of a stack. In chapter 5 we zoomed out further to derive the diffraction spectrum of an aggregate, a system built of \( N \) single particles. Finally, in this section we will zoom out even further and as a result we will look at a system built of aggregates. In this chapter we will also study fractal structures, since these often arise during aggregation.

6.1.1 Qualitative explanation

If aggregates all have the same size and if they are relatively far apart, the total diffraction spectrum is equal to that of one aggregate, where the absolute intensity is multiplied with the number of aggregates. However, if the aggregates have different sizes the total diffraction spectrum is the sum of the different contributions of the respective aggregates. We will illustrate the result with the help of figure 6.1. This figure shows two configurations. The first (A) exists of one aggregate of \( N \) particles, whereas the second (B) consists of two widely separated aggregates, one aggregate built of \( N_1 \) particles and the other built of \( N_2 \) particles. However, the total number of particles is equal in both configurations: \( N = N_1 + N_2 \). The diffraction spectrum of the single aggregate (A) has already been derived in the previous chapter. The part of this spectrum depending on the aggregation has been plotted with a dotted line in figure 6.2. The two contributions to the spectrum of the respective aggregates of the second configuration (B) have been plotted in the same figure with a solid line, just like their sum, the total diffraction spectrum of this configuration, which is plotted with a thick solid line.

Since the intensity is proportional to the number of particles within the aggregate for large \( q \)-values, the sum of the two contributions of the respective aggregates (B) is equal to the intensity of the single large aggregate (A)
Figure 6.1: The configuration of respectively one aggregate (A) and polydisperse aggregates (B).

Figure 6.2: A schematical plot of the cause of a lower slope in the diffraction spectrum (thick) of polydisperse aggregates (configuration B in figure 6.1). As a reference, the diffraction spectrum (dotted) of the single aggregate (configuration A) is also given.
in the large-\(q\) region. On the contrary, the intensity is proportional to the square of the number of particles for \(q \to 0\). Thus in configuration B, the contribution of the small aggregate will be negligible to that of the larger aggregate. As a result, the total diffraction spectrum of configuration B will be proportional to the square of the number of particles in the largest aggregate \(N_1^2\). Thus, in this diffraction spectrum three regions can be discerned, namely region \(a\) contributed to by the largest aggregate, region \(c\) as a result of both aggregates and finally region \(b\) where the result of polydispersion can be seen as a lower slope in the plot.

### 6.1.2 Schultz distribution

In a real system there are not just two aggregates, but such system will consist of many more aggregates, all having their respective size. These sizes of the aggregates can be described by a distribution function of their respective radii. It is known from thermodynamics that in a polydisperse cluster system there are many more small clusters than large clusters. However, the scattering intensity in the small-\(q\) range is dominated by the contribution from the large clusters. As a result, the scattering intensity is largely due to the 'dilute' large clusters, which are 'dispersed' in a sea of small clusters. Thus from the scattering-intensity point of view, the arrangement is equivalent to a dilute system. Consequently we can neglect the interaggregate interference and the total scattering intensity is equal to the sum of the separate aggregate contributions.

\[
I(q) = \int_0^\infty dR f(R) I_{\text{aggregate}}(q, R),
\]

where \(f(R)\) is the distribution function for the sizes of the aggregates.

Sheu [9] has given the spectrum in case of spherical particles with radii distributed according to the Schultz distribution. This two-parameter distribution function is given by

\[
f_s(R) = \frac{1}{\Gamma(z + 1)} \left[ \frac{z + 1}{R_g} \right]^{z+1} \frac{R^z \exp \left[ - \left( \frac{z + 1}{R_g} \right) R \right]}{R_g},
\]

where \(R_g\) is the average radius of the spherical aggregates and \(z\) is the width parameter, characterizing the degree of polydispersion of the aggregate sizes. Low values of \(z\) result in a large polydispersion, whereas the Schultz distribution tends to a Gaussian form at large \(z\) values and approaches a delta function as \(z\) goes to infinity.

The result Sheu obtained, which we have not checked, is:

\[
\begin{align*}
I_S(q) &= 8\pi^2 R_g^6 (z + 1)^{-6} \alpha^{z+7} J(q), \\
J(q) &= \alpha^{-(z+1)} - (4 + \alpha^2)^{-(z+1)/2} \cos(\chi_1) \\
&\quad + (z + 1)(z + 2) \left[ \alpha^{-(z+3)} + (4 + \alpha^2)^{-(z+3)/2} \cos(\chi_3) \right] \\
&\quad - 2(z + 1)(4 + \alpha^2)^{-(z+2)/2} \sin(\chi_2),
\end{align*}
\]
\[ \chi_I = (z + i) \tan^{-1}(2/\alpha) \text{ and } \]
\[ \alpha = \frac{(z + 1)}{qR_g} \]

This function has been plotted for two values of \( z \). Namely in figure 6.3 for a large value, \( z = 10,000 \), and in figure 6.4 for a small value, \( z = -0.9 \). In both cases \( R_g = 10 \). The spectrum of the former approaches the spectrum derived for a single sphere (see figure 3.2). This is a good thing since for this \( z \)-value the distribution function approaches a delta function, so all spheres have the same size.

![Figure 6.3: The distribution function for \( z=10,000 \) (left) and the corresponding spectrum (right).](image)

In contrast, the latter spectrum is smooth with a slope \(-4\). The distribution function shows that the smaller particles are, the larger the number of these within the system. However the contribution to the spectrum is proportional to the square of their volume. Figure 6.5 shows the relative importance of all particles with a certain radius in the system. As can be seen the particles of radius 300-800 give the largest contributions, whereas the rest is negligible. This means that only for \( q < 0.006 \) a smaller slope can exist, whereas for larger \( q \)-values the slope \(-4\) continues to exist. The spectrum is smooth because it is the sum of different contributions each having their minima at different \( q \)-values.

The conclusion is that we need a distribution function which yields even more small particles to obtain a lower slope. We will see one in section 6.3.
Figure 6.5: A plot of $r^6 f_s(r)$. Since the intensity is proportional to the square of the volume, this function gives the relative importance of the spheres of radius $r$ within the polydisperse system.

The result Sheu obtained for polydisperse solid spheres can be inserted into our model. In fact, in case of a spherical aggregate built of discs, the distribution function describing the distances between the centers of mass of the discs (see 5.21) is the same as Sheu used to describe a solid sphere. Thus we can insert the above theory of polydispersion in our model, yielding a model for a system of polydisperse aggregates built of discs, where the radii of the aggregates are distributed according to the Schultz distribution:

$$< I(q) >_q = N \frac{2V^2}{(qR)^2} \left( 1 - \frac{1}{qR} J_1 (2qR) \right)$$

$$+ N(N-1) \sum_{l=0}^{\infty} \frac{4V^2}{(qR)^4} < P_{2l}(\mathbf{n}_1 \cdot \mathbf{n}_2) >$$

$$\times \left[ \sqrt{4l+1} \frac{(2l)!}{4l(l)!^2} \int_0^{qR} d(qr) (qr) j_{2l}(qr) \right]^2$$

$$\times I_S(q).$$

The correlation coupling can be tuned on and off again with the help of the order parameter, like we have seen for one such aggregate. However, if we omit the orientation correlation of the discs, since this appeared to have only little influence on the diffraction spectrum, this yields the simplification:

$$< I(q) >_q = N < I_{\text{disc}}(q) >_q$$

$$+ N(N-1)I_S(q) < I_{\text{disc}}(q) >_q. \quad (6.5)$$

### 6.2 Fractal aggregates

It is well known that the structures that come into being during aggregation, are not uniform, but may have a fractal mass distribution. The origin of this phenomenon has been outlined in figure 6.6. In the beginning, all particles are loose and move in a random direction, e.g. by Brownian motion.
Figure 6.6: During aggregation fractal structures come into being.

When two particles collide there is a certain chance that those particles stick together. If they do so, they will go on together like one particle. In that way small aggregates arise, which will collide with each other again, finally yielding one large fractal aggregate.

In order to describe such an aggregate, we will use the distribution function of solid spheres within a spherical aggregate. In a $D_m$-dimensional space, the number $N(r)$ of primary particles, of radius $R$, within a spherical aggregate of radius $r$ is given by $N(r) = (r/R)^{D_m}$. The derivative of this equation can be related to the asymptotic pair-correlation function $g(r)$ through the relation

\[ g(r) = \frac{1}{4\pi r^2} \frac{dN}{dr} = \frac{D_m}{4\pi N_v} \frac{1}{R^{D_m}} r^{D_m-3}, \]  

where $N_v$ is the number of primary particles per unit volume. This will be the correct asymptotic behaviour of $g(r)$ for $r >> R$ in an infinite system. However, in our model, we expect the correlation to have a limited range. Therefore, the correlation will have a finite range $\chi$ and we introduce the cutoff factor $\exp(-r/\chi)$. This method has been suggested by Schmidt [8].

The expression for $I_F(q)$ now follows from

\[ I_F(q) = N_v \int_0^\infty dr \frac{4\pi r^2 g(r)}{q} \frac{\sin(qr)}{qr} \]  

This integral is a 'standard' integral which can be solved analytically, see for example [12]. This results in

\[ I_F(q) = \frac{D_m}{(qR)^{D_m}} \frac{\Gamma(D_m - 1)}{[(q\chi)^{-2} + 1]^{(D_m-1)/2}} \sin \left[ (D_m - 1) \tan^{-1}(q\chi) \right]. \]  

We will now take $\chi$ equal to the radius of the aggregate, which itself is equal to $RN^{1/D_m}$. Filling this into equation 6.8 and normalising it properly to
CHAPTER 6. POLYDISPERSE AND FRACTAL SYSTEMS

obtain $I_F(q) = 1$ for $q \to 0$, results in

$$I_F(q) = \frac{\sin \left( (D_m - 1) \tan^{-1}(qx) \right)}{(D_m - 1)(qx)[1 + (qx)^2]^{(D_m-1)/2}}.$$  \hspace{1cm} (6.9)

This theory can be inserted into our model by using formula 6.6 as the distribution function of the centers of mass of the discs. Again omitting the orientation correlation of the discs, the result for a fractal aggregate built of discs now states

$$< I(q) >_q = N < I_{\text{disc}}(q) >_q$$

$$+ N(N-1)I_F(q) < I_{\text{disc}}(q) >_q.$$ \hspace{1cm} (6.10)

6.2.1 Graphical representation and simulation

Equation 6.9 results in a spectrum showing a slope $-D_m$ when $D_m < 3$. However, when $D_m \approx 3$ we reach a singular point, since for $q > 1$, the argument of the sine approaches to $\pi$ and a slope $-4$ arises instead of a slope $-3$. In figures 6.7 this is shown for two different fractal dimensions, namely $D_m = 1.7$ and $D_m = 3$.

![Figure 6.7: $I_F(q)$ of a spherical aggregate with respectively $D_m = 1.7$ (left) and $D_m = 3$ (right).](image)

We can also verify this result numerically. In order to do so, we need a fractal with a known fractal dimension. An example of such a fractal structure is a so-called Vicsek fractal. The way such a fractal is constructed can be seen best from a 2-dimensional Vicsek fractal. That fractal is shown in figure 6.8. If we look at this example we see that by multiplication of the radius $r$ with a factor 3, the mass $M$ within that radius enlarges with factor 5. Therefore the fractal dimension $D_m$ of a 2D-Vicsek fractal is $\log 5/\log 3 = 1.465$. In the same way, a 3-dimensional Vicsek fractal can be constructed. Such fractal is given on the left hand side in figure 6.9. The fractal dimension of such a fractal is $D_m = \frac{\log 7}{\log 3} = 1.77$, since in this case the mass enlarges with a factor 7 when the radius is multiplied with a factor 3.

As we can see on the right hand side of the same figure the diffraction spectrum shows a slope $-D_m$ indeed. However, this slope is not smooth. This can be understood since a Vicsek fractal is very regular, because of which some preferential distances will occur.
6.3 Polydisperse fractal aggregates

Of course we can also have a polydisperse system of fractal aggregates. Thus, the next step we will make is to derive the diffraction spectrum of such a system. The total spectrum will again be given by the summation of contributions of all individual aggregates. First, we have to look for an appropriate form for the distribution of aggregate sizes. Following Stauffer [13], we will use

\[ f(N) \propto N^{-\tau} \exp(-N/S), \]

which is a distribution function occurring naturally for fractal aggregation. In this formula \( N \) is the number of discs within the aggregate, \( S \) a measure of the average number of discs within the aggregate and \( \tau \) an index representing the degree of polydispersity of the aggregate sizes. A smaller \( \tau \)-value means a broader aggregate size distribution. Normalizing the total mass,
\[ f(N) = \frac{S^{\tau-2}N^{-\tau}}{\Gamma\left(2 - \tau, \frac{1}{S}\right)} \exp\left(-\frac{N}{S}\right), \]  

(6.12)

where \( \Gamma(a, b) \) is the incomplete gamma function.

The total scattering now becomes:

\[ <I(q)> = \int_{N=1}^{\infty} dN \frac{f(N)}{N} \left[J_{\text{disc}}(q, R) + N(N-1)I_{\text{aggregate}}(q, d)\right]. \]  

(6.13)

The contribution of one disc to the total diffraction spectrum is independent of the total number of discs within the aggregate. The integration of the first part thus simply yields \( I_{\text{disc}}(R) \), since \( \int dN f(N) \) has been normalized to unity. When we further use \( I_F(q) \) from equation 6.9 for \( I_{\text{aggregate}} \), the total diffraction spectrum becomes

\[ <I(q)> = \frac{2V^2}{(qR)^2} \left(1 - \frac{J_1(2qR)}{qR}\right) + V^2 \int_1^\infty dN N(N-1) \frac{S^{\tau-2}N^{-\tau}}{\Gamma\left(2 - \tau, \frac{1}{S}\right)} \exp\left(-\frac{N}{S}\right) \]

\[ \times \frac{\sin\left[(D_m - 1)\tan^{-1}(qR_N)\right]}{(D_m - 1)(qR_N)\left[1 + (qR_N)^2\right]^{(D_m - 1)/2}}, \]

where \( R_N \) is the radius of an aggregate consisting of \( N \) discs. The integral occurring in this equation cannot easily be solved analytically. But it can be solved by approximating the spectrum for the low \( qR_N \) values by

\[ I_F^{(1)}(q) \approx e^{-D_m(D_m+1)q^2R_N^2/6} \]  

(6.15)

and, on the other hand, approximating it for the high \( qR_N \) values by

\[ I_F^{(2)}(q) \approx \frac{\sin\left[(D_m - 1)\frac{5}{2}\right]}{(D_m - 1)(qR_N)^{D_m}}. \]  

(6.16)

This approximation, which corresponds to the limiting values of large and small \( q \), has been elaborated by Chen [14].

For \( N^2 \) instead of \( N(N-1) \) the integral now shows

\[ \int_1^{(qR)^{-D_m}} dN \frac{s^{\tau-2}N^{2-\tau}}{\Gamma\left(2 - \tau, \frac{1}{S}\right)} e^{-\frac{N}{S}} I_F^{(1)}(q) \]

\[ + \int_{(qR)^{-D_m}}^\infty dN \frac{s^{\tau-2}N^{2-\tau}}{\Gamma\left(2 - \tau, \frac{1}{S}\right)} e^{-\frac{N}{S}} I_F^{(2)}(q). \]  

(6.17)

Rewriting the first of these integrals to a new integration variable yields

\[ \frac{s}{\Gamma\left(2 - \tau, \frac{1}{S}\right)} \int_{(1+x^2)^{D_m/2}}^u dy y^{2-\tau} \]

\[ \times e^{-\left[y(1+x^2)^{D_m/2}+x^2(1+y^2)^{-1}y^{3/D_m}\right]}(1 + x^2)^{-D_m(3-\tau)/2}, \]  

(6.18)
where
\[ u = \left[ \frac{h^2(1 + x^2)}{x^2} \right]^{D_m/2} \] (6.19)

while evaluation of the second integral yields
\[ \frac{s}{\Gamma(2 - \tau, \frac{x}{h})} \Gamma \left(2 - \tau, \left[ \frac{x}{h} \right]^{-D_m} \right) \left[ \frac{x}{h} \right]^{-D_m} \sin \left[ \left( D_m - 1 \right) \frac{\pi}{2} \right] \frac{\sin \left[ \left( D_m - 1 \right) \frac{\pi}{2} \right]}{\left( D_m - 1 \right)}. \] (6.20)

In the following the average aggregate size \( s \) will be assumed to be large, thus making \( 1/s \) to approach zero. In that case the remaining integral in the former expression is equal to the gamma function \( \Gamma(3 - \tau) \) minus its incomplete gamma function \( \Gamma(3 - \tau, u) \) for \( D_m = 2 \), while for other values of \( D_m \) this only holds in a first approximation.

Using these results in our equation 6.14 yields the total diffraction spectrum of a system of polydisperse spherical aggregates built of discs
\[ < I(q) > q = \frac{2V^2}{(qR)^2} \left(1 - \frac{J_1(2qR)}{qR} \right) \]
\[ + \frac{s}{\Gamma(2 - \tau)} F(3 - \tau, q\xi) \left[1 + (q\xi)^2\right]^{-D_m(3-\tau)/2} \]
\[ + \frac{s}{\Gamma(2 - \tau)} G(2 - \tau, q\xi) \left[ \frac{q\xi}{h} \right]^{-D_m}, \]

where \( \xi \) is the correlation length, defined as \( \xi = hRS^{1/D_m} \),
\[ F(a, x) = \Gamma(a) - \Gamma(a, u), \quad \text{where} \]
\[ u = \left[ \frac{h^2(1 + x^2)}{x^2} \right]^{D_m/2} \quad \text{and} \]
\[ h = \sqrt{\frac{D_m(D_m + 1)}{6}}. \]

Further, the function \( G(a, x) \) is given by
\[ G(a, x) = \sin \left[ \frac{(D_m - 1)\pi}{2} \right] \frac{\Gamma \left( a, \left( \frac{\xi}{h} \right)^{-D_m} \right)}{D_m - 1}. \] (6.23)

The diffraction spectrum in equation 6.21 consists of three contributions. One because of the primary particles and two because of the aggregation. Here we will concentrate on the latter. In the large-\( q \) region one of those two terms is proportional to \( q^{-D_m(3-\tau)} \), whereas the other is proportional to \( q^{-D_m} \). The term with the lowest power will dominate, respectively resulting in a slope \( -D_m(3 - \tau) \) in case \( \tau > 2 \) and a slope \( -D_m \) in case \( \tau < 2 \). This is plotted in figure 6.10 for aggregates of fractal dimension \( D_m = 2.7 \), once for \( \tau = 1.5 \) and once for \( \tau = 2.5 \).

In case \( D_m \) approaches to 3, function \( G(a, x) \) becomes zero because of the sine term, a problem we have seen before. However, because of the
polydispersity of the aggregates a second term has turned up, which differs from zero and which depends on a combination of $\tau$ and $D_m$. A special case would occur for $\tau = 2$. For this value of $\tau$, the slope of the spectrum, for $R < q^{-1} < \chi$, would again be equal to the fractal dimension of the aggregate, even for $D_m = 3$. But, $\tau = 2$ corresponds to a, in percolation theory well known, singularity in the aggregate size distribution function 6.12. However, an important conclusion we can make here is that a slope close to $-3$ occurring in a diffraction spectrum can occur from a combination of $D_m$ and $\tau$, since $\tau$ can be close to 2. For example, for random percolation $\tau = 2.2$. 

Figure 6.10: The diffraction spectra of polydisperse fractal aggregates ($D_m = 2.7$) in case respectively $\tau = 1.5$ (left) and $\tau = 2.5$ (right).
Chapter 7

Using the model

In the previous chapters we have derived a theoretical model for the diffraction spectrum of an aggregate built of discs. Further, we extended the model to enclose polydisperse and/or fractal aggregates. In this chapter we will show how we can use our model to interpret experimental spectra. Three aspects of a spectrum will play a major role, namely:

- the slopes in the spectrum,
- the positions (q-values) of the kinks (the transitions between two slopes) and
- the absolute intensity of the horizontal parts in the spectrum.

7.1 The spectrum

Like derived in chapter 5, the total diffraction spectrum of a spherical aggregate of discs is given by 5.21, namely:

\[
\langle I(q) \rangle_q = N I_{disc}(q, R) + N(N-1)I_{agg}(q, d),
\]

where \( q \) is the scattering vector, \( R \) the radius of a disc, \( N \) the number of discs within the aggregate, and \( d \) the radius of the spherical aggregate.

So, there are two contributions to the diffraction spectrum. The first term arises because of the separate discs (intraparticle scattering), whereas the second arises because of the interaction between different discs (interparticle scattering). These two terms and the total diffraction spectrum have been plotted in figure 7.1. The former is proportional to \( NV^2 \), whereas the latter is proportional to \( N^2V^2 \), where \( V \) is the volume of one disc.

From this figure it is obvious that the spectrum can be split in two parts. In each \( q \)-range one contribution dominates the other. The large-\( q \) region describes the building blocks, whereas the small-\( q \) region describes the aggregate. In order to interpret the diffraction spectrum we will outline it with lines of slope 0, -2 and -4 respectively. Such a schematic plot has been given in figure 7.2. The three characteristics mentioned above, namely
7. USING THE MODEL

Figure 7.1: The two contributions (left) and the total diffraction spectrum (right) of a spherical aggregate of discs.

the slopes, the kinks and the intensities appear clearly in such a plot. We will use the rest of this chapter to show what these characteristics can tell us about the structure we want to analyse.

Figure 7.2: Outline of the diffraction spectrum in order to determine the q-values of the kinks, the slopes, and the intensities of the horizontal parts of the spectrum.

7.2 Kinks

In analysing an experimental diffraction spectrum it is important to be able to determine some length scales easily. In the case of the model just derived, we want to know the radius of the aggregate \( d \), but also the radius of the primary particles \( R \), the discs, and their number within the aggregate \( N \).

In the first place we will derive a relation between the radius of the sphere, the aggregate, and the q-value of the kink which describes this radius. The relation we want to derive is of the form

\[
q_s R_s = s = \text{Constant}, \tag{7.2}
\]

where \( q_s \) is the q-value where the lines of slope 0 and \(-4\) cross, \( R_s \) is the radius of the sphere and \( s \) is a constant we are looking for. The q-value
where the line of slope $-4$ crosses the second horizontal line is marked in the plot as $q_e$. This is the point where the two contributions to the diffraction spectrum, namely the interpartiele and intrapartiele contribution, are equal. This point (see equation 5.24) can be given by the relation

$$9(N - 1) = (q_e R_s)^4.$$  

(7.3)

Combination of 7.2 and 7.3 results in the relation

$$9(N - 1) = (q_e^4 q_s^4).$$  

(7.4)

Because $q_s$ and $q_e$ in figure 7.2 are connected by a line of slope $-4$, a second relation between these to $q$-values can be given, namely by

$$-4(\log q_e - \log q_s) = \log N - \log N^2,$$  

(7.5)

which can be rewritten as

$$\left(\frac{q_e}{q_s}\right)^4 = N.$$  

(7.6)

From equations 7.3 and 7.6 now follows that, for $N \gg 1$, $s = \sqrt{3}$. So now we have derived a relation to determine the radius of a sphere directly from its diffraction spectrum by:

$$q_s R_s = \sqrt{3}.$$  

(7.7)

The same kind of derivation is possible for a disc or for a rod-like particle. In case of a disc this results in the relation

$$q_d R_d = \sqrt{2}$$  

(7.8)

and in case of a rod-like particle the relation shows

$$q_r H_r = \frac{\pi}{2}.$$  

(7.9)

In these relations, $R_d$ is the radius of a disc and $H_r$ is the half height of a rod-like particle. Thus, we can conclude that for the position of the kink holds $qL \approx 3$, where $L$ is the largest distance within the particle.

The number of particles within the aggregate can be determined by the positions of the kinks using equation 7.4. Since we have also determined the radius of the aggregate and the radius of the primary particle, this yields the density too.

### 7.3 Slopes

Figure 7.2 shows four parts of the spectrum. The first part has a slope 0. The length scale we are looking at here is large compared to the size of an aggregate. Thus, its shape cannot be discerned and the intensity is proportional to the square of the diffracting mass, $N^2 V^2$. The slope in the second region (b) and the fourth region (d) describe respectively the aggregate and the primary particles, the discs. The width of the third region
CHAPTER 7. USING THE MODEL

(c), which also has a slope 0, depends on the density of the aggregate, as shown in the previous section. Thus, two slopes, different from 0, appear in the spectrum. The magnitude of these slopes can result from three different origins, namely

- the shape of the particle/aggregate,
- the internal structure of the particle/aggregate and
- polydispersity.

In chapter 3 the influence of the shape of particles has been studied. Spherical particles result in slope −4 and discs in a slope −2. However, in the literature more particle shapes have been studied. For example, a rod-like particle results in a slope −1. This can also be inserted into our model.

In chapter 6 we studied the influence of fractal aggregates, which appeared to result in a slope −\(D_f\), where \(D_f\) is the fractal dimension. In the same chapter the influence of polydispersity of the aggregate sizes has been studied. This turned out also to influence the slope. Depending on the distribution of the aggregate sizes a lower slope can occur than would be expected from the shape or structure of one individual aggregate.

### 7.4 Intensities

The last characteristic mentioned is the value of the absolute intensities of the two horizontal parts in the spectrum. For \(q \to 0\), region (a) the length scale we are looking at is large compared to the size of the aggregates. As a result, neither the internal structure nor the shape of the aggregates can be seen and the spectrum is only determined by the quantity of scattering mass, \(N^2V^2\).

In region (c), we are looking at length scales small compared to the aggregate size but still large compared to the primary particles. Thus, the shape of the primary particles cannot be determined yet, but the intensity is given by the number of primary particles times the quantity of scattering mass within one particle, thus \(NV^2\).

### 7.5 Conclusion

Concluding, we can say that several aspects of the structure can be determined easily by looking at the diffraction spectrum. However, it is very important to notice that there are also some characteristics in a spectrum that can arise because of different reasons. For example, there are three possible reasons for the appearance of a slope in the spectrum. As a result, the structure cannot be determined as a simple inversion of the spectrum, but all possibilities have to be considered.
Chapter 8

Literature data

In this chapter we will give a survey of the SAXS data on asphaltene mixtures that we have found in the literature. Thereupon, we will compare these data with our model.

8.1 Survey

In the (recent) past, several studies have been performed on the structure of asphaltenes by means of Small Angle X-ray or Neutron scattering. Some results can be found in the literature. A survey is given below:


It has to be noticed that most studies have been performed on solutions of asphaltenes and that most plots of $I(q)$ do not have a double logarithmic scale because of which a lot of information has been lost. Only the first three articles contain double logarithmic plots. In the next section we will not evaluate all spectra completely, but we will compare two of these spectra with our model.

8.2 Comparison with our model

In this section we will give two plots of diffraction spectra, which we found in the first article mentioned above. The study in this article has been performed by D. Espinat et al.. For their experiments, they have used a Middle-East crude, called Safaniya. During vacuum distillation the volatile components of the crude oil evaporate and are separated. The heaviest particles, which are the least volatile, remain behind. This part of the crude that remains behind after vacuum distillation is called the Vacuum Residue. It consist of a complex mixture of thousands of molecules with a wide distribution of molecular sizes and chemical structure. This mixture can be separated into pseudocomponents such as coke, asphaltenes and resins by means of their solubility. This is schematically shown in figure 8.1. In fact,

![Figure 8.1: Separation of Vacuum Residue into coke, asphaltenes and resins.](image)

coke is defined as the insoluble part of the Vacuum Residue in toluene (an aromatic solvent), and asphaltenes are defined as the part soluble in toluene and insoluble in n-heptane (a paraffinic solvent). Finally, resins are defined as the heptane soluble part. For us it is important that resins are known to have molecular weights of 500–2000, whereas asphaltenes have molecular weights of 1000–10,000.
8.2.1 Asphaltene solution

Once the resins and asphaltenes have been separated, they can be dissolved in toluene. In this section, we will treat the diffraction spectra of respectively such an asphaltene solution and such a resin solution. These diffraction spectra are shown in figure 8.2. Next, the diffraction spectrum of the pure Vacuum Residue (VR) will be treated, which is given in figure 8.3.

Figure 8.2: SAXS-spectra of respectively a 6% w/w asphaltene solution (1) and a 6% w/w resins solution (2) in toluene.

Figure 8.2 shows the spectra of respectively a 6% w/w asphaltene and a 6% w/w resins solution in toluene. Most striking is that two regions can be distinguished in both spectra. These regions are roughly separated at $Q_1$. We have seen exactly these two regions in our model, one describing the primary particles and one describing the aggregates. Thus, it is clear with which part of our model we have to compare these experimental data. Notwithstanding this similarity there are also some differences between the two spectra shown. These differences can be summarized by three characteristics, namely going from small-$q$ values towards high-$q$ values: the position of the transition from aggregate dominated spectrum to primary particle dominated spectrum ($Q_1$), the absolute intensity of the horizontal part of the spectrum ($q \approx 10^{-2} \text{Å}^{-1}$) and finally the position of the kink describing the size of the primary particles.

The size of the primary particles can be determined by the position of this last kink since the radius of the particles is inversely proportional to this $q$-value. In case of resins the $q$-value of this kink is about $0.09 \text{ Å}^{-1}$, whereas in case of asphaltenes the $q$-value is about $0.02 \text{ Å}^{-1}$. Thus, according to the model, resins are smaller than asphaltenes, when they are dissolved in toluene. Thus, the volume of resin particles is smaller than the volume of asphaltene particles. This is in accordance with the molecular weight distribution which we have seen before.

We have seen that the size of the primary particles does not only determine the position of the kink described above, but that it also affects the
absolute intensity of the spectrum and the value of \( Q_1 \). This can be understood in the following way. Since both solutions contain the same amount of dissolved matter, namely 6% w/w, \( NV \) is equal in both cases, where \( N \) is the number of particles and \( V \) the volume of one such particle. Thus the smaller the primary particles, the larger the number of them in the solution. The larger the number of particles, the closer they will be together and as a result, the larger the value of \( Q_1 \). This implies that, according to our model, we expect a larger the value of \( Q_1 \) for the resins than for the asphaltenes.

Further, in our model we have seen that the intensity of the horizontal part in the spectrum is proportional to \( NV^2 \). Since \( NV \) is still constant this implies that the smaller the particles, the lower the intensity of the horizontal transition region. Thus, according to our model we expect the intensity of the horizontal part to be smaller for the resins than for the asphaltenes.

Concluding, we can say that the size of the primary particles can be determined by the \( q \)-value of the respective kink and that, according to our model, the difference in size of the primary particles in the two cases has another two consequences to the spectrum, namely the absolute intensity of horizontal transition zone and the value of \( Q_1 \). Both consequences according to our model can be verified in the spectra in figure 8.2.

Now we have explained the \( q \)-values of the kinks and the intensities, this leaves us with the explanation of the slopes. However, since we do not have the real data it is hard to fit slopes. For this reason, we will not go further into this.

### 8.2.2 Vacuum Residue

In figure 8.3 the diffraction spectrum of Safaniya Vacuum Residue has been given for different temperatures. It turns out that the spectrum does not

![Figure 8.3: The diffraction spectra of Pure Safaniya VR at temperatures \( \leq 100^\circ C \) (1) and at 200\(^\circ C \) (2).](image)

change when it is heated from room temperature to 100\(^\circ C\). But, when the
temperature rises above $100^\circ C$ the spectrum changes slightly. However, the data is too indistinct to be able to give a proper explanation. But it is a typical example of a diffraction spectrum, where once again the two regions can be discerned.

### 8.3 Conclusion

As a conclusion of this chapter, we can say that our model can explain the diffraction spectrum found in the literature. But, we can also conclude that there are hardly any proper data in the literature, which cover a sufficient large range and which are given on log-log scale. Especially since we are interested mostly on residues instead of solutions. Thus, since there are scarce data available in the literature to qualitatively fit our aggregate model, we will evaluate in-house (Shell) small angle X-ray scattering data on residues in the next chapter.
Chapter 9

Application to residues

9.1 Survey of used samples

In this chapter we will use our model to interpret some experimental data sets which have been measured on residues. The measurements have been performed on samples taken from:

- **Arabian Heavy SR + 3 TCR’s:**
  Arabian Heavy (AH) is a standard Middle-East crude. The Short Residue (SR) is that part of the crude remaining after vacuum distillation. This residue can be cracked thermally, yielding the Thermally Cracked Residues (TCR’s). The difference between the 3 TCR’s is the time during which they have been cracked.

- **A deviating crude:**
  It is known that crudes from different regions can have a very different composition, not at least since they can have a different origin. (For example whether they originate from land or sea.) For this reason a deviating crude has been chosen to compare its structure with that of the standard Arabian Heavy.

Since this report is about the determination of structures with the help of small-angle X-ray scattering, we will stick to this subject. As a result, in this report we will not investigate the thermodynamics behind these structures.

9.2 The standard: Arabian Heavy

We will start with the description of the data as measured on Arabian Heavy, since this is the standard crude.

At two different locations, X-ray diffraction spectra have been measured, namely in Daresbury and in Grenoble. These measurements have been performed on the same samples, however in another q-range and at another time. In Daresbury measurements have been performed in the range \(0.1 \leq q \leq 2.1 \text{ nm}^{-1}\) whereas in Grenoble in the range \(0.03 \leq q \leq 0.6 \text{ nm}^{-1}\). These two intervals show a certain overlap, because of which the spectra can be
normalised, yielding one large spectrum with a range \(0.03 \leq q \leq 2.1 \text{ nm}^{-1}\). With \(qL \approx 2\pi\) this means that we can determine the structure on length scales \(3 \leq L \leq 200 \text{ nm}\).

The spectrum of Arabian Heavy Short Residue (AH SR) is shown in figure 9.1 (left). The first problem we meet is that both contributions to the spectrum, from Daresbury and Grenoble, are not identical in the range of the overlap. A possible explanation is the fact that these respective spectra have not been measured at the same time, but about half a year apart. Thus, in case the residue is unstable, the chance of finding a (slightly) changed structure is large. However, since both contributions do still show a lot of resemblance in the region of overlap, we will consider the two contributions together to be one spectrum. And we will compare this spectrum with our model.

The next question is with which part of our model we have to compare this spectrum. Thus whether we see the whole spectrum, as well the aggregates as the primary particles, or only part of it. In this case this can be determined by zooming in on the largest \(q\)-values, thus on the smallest structures. This has been done in figure 9.1 (right). In this figure we see a continuously decreasing slope, which finally approaches a horizontal line. (This is something we will see even better for other samples later.) This part of the spectrum corresponds to the transition, in our model, between the regions where respectively the aggregates and the primary particles are described. Thus, the conclusion we have to draw from this is that the primary particles are too small to be described in the experimental spectrum, and consequently, that the spectrum only shows the aggregates.

9.2.1 The primary particles

Since the primary particles cannot be seen in the spectrum, we have to make an assumption about their geometry.
Yen's model

In chapter 1.1 we have already seen a model for the molecules, the primary particles, of asphaltenes, namely Yen's model. This model starts from the principle that asphaltene molecules are flat molecules which can be considered as discs. Further, according to this model, these discs can, depending on their surroundings, form stacks, which in turn can aggregate to yield large structures.

To start with, we will use this model of Yen. The flat molecules are built of an aromatic core, which consists of 8–16 C-rings, and some side chains. A typical example of such a molecule has been shown in figure 1.1. However, in the following we will consider an idealized molecule, built of 12 C-rings without side chains. Such an idealized, symmetrical molecule is shown in figure 1.1. According to this figure the radius of such a disc can be estimated at 0.5 nm.

The diffraction spectrum of one such symmetrical disc, which has been calculated with PARSTRUC, has been plotted in figure 9.3. In the same

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![Figure 9.2](image1.png)

Figure 9.2: One idealized disc-like asphaltene molecule according to Yen's model.

![Figure 9.3](image2.png)

Figure 9.3: Diffraction spectrum of the idealized disc-like molecule, as calculated with ParStruc.
plot, the asymptotes for respectively $q \to 0$ and $q \to \infty$ have been plotted. These asymptotes have respectively a slope 0 and a slope -2. The point of intersection of these two asymptotes has been given by the relation $q_{kink} R = \sqrt{2}$ (equation 7.8), where $R$ is the radius of the disc. Thus, the $q$-value of the kink is expected to lie around $q \approx 3$, which can be validated in figure 9.3. Thus, we can conclude that the kink caused by the basic sheets cannot be seen in the experimental data indeed, not to mention the slope -2, which would arise for even higher $q$-values. Thus, so far Yen's model does not contradict our data.

The next aspect of Yen's model is the possibility of stacking, because of which the separate discs can form stacks of about 4-5 layers. The distance between two successive discs in such a stack is according to Yen about 0.35 nm. We would expect to see this 'interdisc distance' in the diffraction spectrum. However, since $q L \approx 2 \pi$, the distance is too small to be seen in the SAXS spectrum. But it will have a result at higher angles, thus, it should appear in the Wide Angle X-ray Scattering (WAXS) spectrum. In the experimental WAXS data, taken simultaneous with the SAXS data, a peak can be seen around $2\theta = 16^\circ$ indeed. This peak corresponds to a distance of $\pm 0.5$ nm, which we will consider to be our 'interdisc distance'.

![Figure 9.4: WAXS spectrum as measured on Arabian Heavy Short Residue, which shows as peak around $2\theta = 16^\circ$.](image)

The influence of stacking

We will show that stacking yields a peak in the WAXS-data at the proper angle $2\theta$. Further, we will study the influence of the interdisc distance, the number of discs in a stack, the size of the discs and the influence of polydisperse interdisc distances to the position and width of the peak. We will do so by simulating the different spectra with ParStruc.

First we will study the influence of the distance between two successive discs. For this purpose we have built four stacks, each containing five of the discs that we saw in figure 9.2 and each with its own interdisc distance, which varied from 3 Å to 6 Å. These stacks are shown in figure 9.5. It
appears that both the position of the peak and its width depend on the interdiscs distance. The smaller the interdisc distance, the larger the angle $2\theta$ and the wider the peak. But from standard scattering literature it is also known that their ratio, $2\theta/\Delta\theta$, is constant, namely:

$$\frac{2\theta}{\Delta\theta} = n, \quad (9.1)$$

where $n$ is the number of discs in the stack, $2\theta$ the position of the kink and $\Delta\theta$ the width at half height.

The second influence we will study is that of the number of discs in a stack. In figure 9.6 stacks of different heights with their respective WAXS-spectra have been given. It is obvious that the larger the stack, the narrower and the higher the peak, while its position remains the same. With the help of relation 9.1 the number of discs in a stack can be calculated ($n_c$). The results are shown in the following table, where they are compared to their real number ($n$).
The reason that the last height is estimated too low is probably the precision which has been used to calculate the spectrum, namely the number of values \(2\theta\) for which the intensity has been calculated. The real height is probably larger, thus the width at half height smaller, resulting in a higher number of stacks. However, we can see that relation 9.1 is a proper relation to determine the height of the stacks.

The interdisc distance and the number of discs in a stack have the largest influence on the WAXS spectrum. Two other properties, namely the size of the discs and polydispersion in the interdisc distance, which we will not elaborate here, appear to have much less influence.

The conclusion of this is thus that the number of discs within a stack and the distance between two successive discs within such a stack can be determined by the diffraction angle where the peak arises and by the width of this peak.

The influence of wax

However, a peak in the WAXS spectrum can have other origins than the stacking of discs we ascribed it to. For instance one might think of alkane, wax crystals, which yield a peak around \(2\theta = 20^\circ\) (corresponding to 4.5Å). The exact position of this peak can be studied using a structure describing respectively crystalline and amorphous decane, generated with the aid of a Molecular Dynamics study by K. Esselink et al. at SRTCA. These structures have been plotted in figure 9.7.

With ParStruc, the WAXS spectra for the two respective situations, crystalline and liquid (amorphous) decane, have been calculated and the results are plotted in figure 9.8. It turns out that the peak arising from the crystalline wax appears at angles larger than \(2\theta = 20^\circ\), thus the peak in the experimental data cannot be explained as a result of the wax within the residue.

9.2.2 Aggregate structure

Using stacks of discs with interdisc distance 0.5 nm as the primary particles we will explain the spectra of the Arabian Heavy samples. Figure 9.9 shows four different spectra, measured on four different samples, each taken at a different moment in the process of thermal cracking.

<table>
<thead>
<tr>
<th>(\Delta \theta (^\circ))</th>
<th>(n_c)</th>
<th>(n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.28</td>
<td>4.25</td>
<td>4</td>
</tr>
<tr>
<td>2.80</td>
<td>6.5</td>
<td>6</td>
</tr>
<tr>
<td>2.18</td>
<td>8.37</td>
<td>8</td>
</tr>
<tr>
<td>1.54</td>
<td>11.8</td>
<td>12</td>
</tr>
<tr>
<td>1.01</td>
<td>18.3</td>
<td>24</td>
</tr>
</tbody>
</table>
CHAPTER 9. APPLICATION TO RESIDUES

Figure 9.7: Cristalline (left) and amorphous (right) decane as generated with a Molecular Dynamics study.

Figure 9.8: WAXS-spectrum of the crystalline and amorphous decane structures as calculated with ParStruc.
Figure 9.9: Diffraction spectra of four Arabian Heavy samples, namely the Short Residue and three thermally cracked residues.

<table>
<thead>
<tr>
<th>Nr</th>
<th>Sample id</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AH SR</td>
<td>Arabian Heavy Short Residue</td>
</tr>
<tr>
<td>2</td>
<td>AH TCR 1</td>
<td>AH thermally cracked during $t_1$</td>
</tr>
<tr>
<td>3</td>
<td>AH TCR 2</td>
<td>AH thermally cracked during $t_2$ ($t_2 &gt; t_1$)</td>
</tr>
<tr>
<td>4</td>
<td>AH TCR 3</td>
<td>AH thermally cracked during $t_3$ ($t_3 &gt; t_2$)</td>
</tr>
</tbody>
</table>

Because the spectra correspond to four different samples, each with its own asphaltene density, we cannot compare the absolute value of the intensities to each other. This means that we have to give an explanation using the other two characteristics of the spectra (see chapter 7), the slopes and the positions of the kinks. So these are summarized below:

**Slopes**

<table>
<thead>
<tr>
<th>Sample id</th>
<th>Grenoble</th>
<th>Daresbury</th>
</tr>
</thead>
<tbody>
<tr>
<td>AH SR</td>
<td>$0.03 \leq q \leq 0.1 : 2.9$</td>
<td>$1.5 \leq q \leq 2 : 1.05$</td>
</tr>
<tr>
<td>AH TCR 1</td>
<td>$0.03 \leq q \leq 0.06 : 2.9$</td>
<td>$0.5 \leq q \leq 1.4 : 1.6$</td>
</tr>
<tr>
<td>AH TCR 2</td>
<td>$0.03 \leq q \leq 0.05 : 2.9$</td>
<td>$0.3 \leq q \leq 1.4 : 1.7$</td>
</tr>
<tr>
<td>AH TCR 3</td>
<td>$0.03 \leq q \leq 0.3 : 2.2$</td>
<td>$0.1 \leq q \leq 1.4 : 1.75$</td>
</tr>
</tbody>
</table>
Kinks

<table>
<thead>
<tr>
<th>Sample id</th>
<th>First kink</th>
<th>Second kink</th>
<th>Third kink</th>
</tr>
</thead>
<tbody>
<tr>
<td>AH SR</td>
<td>0.03</td>
<td>0.6</td>
<td>&gt;2.1</td>
</tr>
<tr>
<td>AH TCR 1</td>
<td>0.03</td>
<td>0.6</td>
<td>&gt;2.1</td>
</tr>
<tr>
<td>AH TCR 2</td>
<td>0.03</td>
<td></td>
<td>&gt;2.1</td>
</tr>
<tr>
<td>AH TCR 3</td>
<td>0.03</td>
<td></td>
<td>&gt;2.1</td>
</tr>
</tbody>
</table>

All spectra show some common features. We already saw that the primary particles cannot be discerned in the AH SR spectrum. This is, for the same reasons, also the case for the other spectra. The second common feature in the spectra is a kink around \( q \approx 0.03 \). However, this kink arises as a result of the measuring method instead of as a result of the structure we want to determine. Namely, in this limit of the \( q \)-range, we look at small angles and the intensity here is lower because part of the scattered rays are stopped by the beam stop, which is meant to stop the part of the incoming beam that has not been scattered.

![Figure 9.10](image)

**Figure 9.10:** Diffraction spectrum of Arabian Heavy: the whole spectra (left) and zoomed in on large-\( q \) region (right).

Other than these general properties, there also occur several differences in the respective diffraction spectra. This can be seen most easily from figure 9.10 (left), where the spectra have been normalized to unity at the right hand side of the spectrum. In the spectrum of the short residue (AH SR), there is a flat part for \( 0.2 \leq q \leq 0.6 \). During cracking a slope \(-1.7\) arises, which is still in a very small range for AH TCR 1, but which covers the whole Daresbury data for AH TCR 3.

A flat part in the spectrum with a kink around \( q \approx 0.6 \) points to aggregates with a diameter of 6 nm, which are relatively small aggregates since the diameter of the primary particles is about 1.5 nm. During cracking these aggregates break done, but a large stucture comes into existence with a fractal dirneusion 1.75. This can be seen by the increasing region in the spectrum in which a slope \(-1.75\) arises.

A possible explanation for this behaviour is given by the following. The core of the asphaltenes is aromatic. This is in contrast to the rest of the residue, which contains mostly carbon-hydrogen chains. As a result, the
asphaltenes do not fit in their environment. However, in the short residue, some other molecules exist, for example resins, that keep the asphaltenes in the solution. They do so because one side of these molecules resembles the asphaltenes, whereas the other fits the carbon-hydrogen chains. But, when the residue is cracked thermally, these smaller resins will disappear first, because of which the asphaltenes cannot be dissolved anymore and start to aggregate into large fractal structures.

9.3 A deviating crude

Also the diffraction spectra of the vacuum residue of a deviating crude has been measured. The respective spectrum is shown in figure 9.11. This crude has a totally different geographical origin as the Arabian Heavy, which comes from the Middle-East. Because of this it also has a different composition. Thus, the question that arises is whether such a different composition may also result in a different structure. Especially since other experiments have shown that its thermodynamic stability is different from that of Arabian Heavy.

The most striking feature of the data is a slope $-1$ in a relatively large range on the right hand side of the spectrum. A slope $-1$ can result from several causes. For example, everywhere where a transition occurs from a slope smaller than $-1$ to a slope larger than $-1$, a slope $-1$ will occur too. However, in figure 9.12 is shown that a slope $-1$ over such a large range as in the data cannot be interpreted as a transition from the horizontal part in the spectrum to the slope characteristic of the shape of the primary particles, like for instance for a sphere.

The only way this slope $-1$ can be interpreted is as a result of a rod-like particle. This means that in this particular case, the primary particles can be seen in the experimental data. This can be understood, since rod-like particles implies large stacks, which in turn implies large primary particles. The height of these stacks can be determined by the position of the kink. This has been determined in figure 9.13. According to the theory, the height is given by $q_{kink}H_r = \pi/2$, where $H_r$ is the half height. Because $q_{kink} = 0.6$, the height of the stack, $2H_r$, is $5.2$ nm. With the assumption that the
interdisc distance is equal to 0.5 nm, this means that the stacks are built of about 10 discs. Thus, this is a typical example of a deviating structure.

Figure 9.12: Comparison of the slope \(-1\) in the data (right) to a ‘slope’ \(-1\) because of respectively a sphere, a disc, a cylinder 1:5 (diameter:height) and a cylinder 1:10 (left).

Figure 9.13: Determination of the height of the stacks by means of the \(q\)-value of the kink.

### 9.4 Conclusion

In this chapter we have studied the diffraction spectra of Arabian Heavy Short Residue and of its thermally cracked residues. We have seen that our diffraction spectra only show the aggregates, whereas the primary particles are too small to be seen. However, with the help of Yen’s model and the WAXS data of the same samples, we have been able to show that the primary particles are stacks of discs. Using these stacks of discs as the primary particles we have seen that the short residue consists of small aggregates, whereas during cracking a large fractal structure comes into existence.

We have also seen a more exotic crude which shows another structure. However, the mechanism shows much similarities. In fact, the asphaltenes from all residues appear to form stacks. Thus, it is advantageous for the discs to stack. The difference is thus the number of discs within a stack.

A possible explanation for the number of discs within a stack can be the
number of side chains. In fact, these side chains are not always perfectly in the plane of the discs. Thus in case each disc has a lot of these side chains, these side chains will hinder the possibility of stacking. This is schematically shown in figure 9.14, where the discs on the left hand side have more side chains than the discs on the left hand side, because of which they cannot form larger stacks, whereas the discs on the left hand side can, essentially, form infinitely high stacks.

Figure 9.14: The influence of side chains on the possibility to form high stacks.
Chapter 10

Simulation

It is striking how often a slope $-1.75$ appears in the experimental data. We have explained this slope as arising from the fractal dimension of the aggregates, since the corresponding fractal dimension $D_m = 1.75$ is equal to that expected in case of diffusion limited cluster-cluster aggregation.

However, since this slope $-1.75$ appears all the time, we will try to achieve this slope also by a numerical simulation with ParStruc. ParStruc only calculates the spectrum of the structure given by the user. So we need another program that can generate the desired structure. In chapter 6 we have already seen that the diffraction spectrum of a Vicsek fractal indeed shows a slope according to its fractal dimension. However, due to cluster-cluster aggregation another kind of fractals will arise. At SRTCA also a computer program is available which describes cluster-cluster aggregation. This program has been developed by P. Hilbers et al. The principle of this program is outlined below.

At the starting point of the simulation $(t = t_0)$, $N$ particles are distributed uniformly within a volume $V_0$. Because of the Brownian movement of the particles, all particles will move and thus have a certain chance of colliding to each other. Every time such a collision takes place, these particles can just collide and move on in another direction, or they can stick together and move on further together like they were one particle. Thus in the beginning $(t = t_1)$ some small aggregates built of 2–3 primary particles will come into being. And the more of these aggregates arise, the larger the chance that such aggregates will collide to each other and stick together to form larger aggregates $(t = t_2)$. At a certain moment some aggregates will have such a size that we can really speak of a fractal structure $(t = t_3)$. If this process keeps on going, eventually all particles will form one large aggregate $(t = t_4)$.

The diffraction spectra of the initial situation, the final structure as well as some intermediate steps have been given in figure 10.1. At $t = t_0$ all particles (64.000) are uniformly distributed within the volume $V_0$, where the concentration was set at 1%. This has been done in a very regular way, because of which it forms a crystal-like structure. As a result, the interparticle distance, which is a preferential distance, can be seen by means
of the two narrow peaks at the right hand side of the spectrum. On the left hand side we see a horizontal part in the spectrum, which is proportional to the square of the total number of scatterers. In between, a slope $-4$ can be discerned. A slope we expected, since here we are looking inside a 3-dimensional uniform system.

A little later, $t_1$, all particles have moved and the crystallike structure has disappeared. As a result the two peaks on the right hand side of the spectrum have disappeared. Like we have seen above, at time $t_2$ some little aggregates have come into being. However, in the diffraction spectrum the slope $-1.75$ cannot be discerned yet, since these aggregates are too small. At $t_3$ the slope $-1.75$ is clearly visible. At this moment some large aggregates exist. The slope $-4$ can still be understood by the uniform distribution of the aggregates within the volume $V_0$. However, when the aggregates grow, the space they need grows too. Namely, since the fractal dimension is about 1.75 such aggregates are airy. The space needed by an aggregate built of $k$ particles is:

$$V_k = \frac{\pi}{6} d_k^3,$$  \hspace{1cm} (10.1)

where $d_k$ is the diameter of the aggregate. This diameter is given by

$$d_k = d_0 k^{1/D_m},$$  \hspace{1cm} (10.2)

where $d_0$ is the diameter of one particle and $D_m$ the fractal dimension. The total space needed by all aggregates is thus

$$V_{tot} = \frac{\pi}{6} d_0 \sum_k M_k k^{3/D_m}.$$  \hspace{1cm} (10.3)

On the other hand, the total volume available is $V_0$. Thus, we can define a parameter $\Phi$, which shows the volume fraction needed by the aggregates. For $t_0$ this parameter was chosen to be 0.01. With the help of the distribution
of aggregate sizes, which is also given by the computer program, the other
volume fractions can be calculated. The result is shown in the table below.

<table>
<thead>
<tr>
<th>time</th>
<th>Φ</th>
</tr>
</thead>
<tbody>
<tr>
<td>t₀</td>
<td>0.01</td>
</tr>
<tr>
<td>t₁</td>
<td>0.01</td>
</tr>
<tr>
<td>t₂</td>
<td>0.03</td>
</tr>
<tr>
<td>t₃</td>
<td>0.14</td>
</tr>
<tr>
<td>t₄</td>
<td>46.99</td>
</tr>
</tbody>
</table>

From the table above, it is clear that when all particles have formed one
aggregate, $t₄$, this aggregate does not fit anymore in the volume $V₀$. However,
the particles are forced to stay within this volume, because of which gelation
takes place. Thus, up to a certain length scale we will expect to find the
fractal structure, whereas on a larger lengthscale we expect to see an uniform
object, with its corresponding slope $-4$.

The next step in our simulation will be to replace every point in the
fractal system ($t = t₄$) by a randomly oriented disc as shown in figure 1.1.
Each disc is built of 37 atoms. Since the calculation is proportional to the
square of the number of particles, the new simulation would take $37² = 1369$
times, thus much too long. Besides, if we would replace all points by stacks
of 5 discs in stead of loose discs, this would cost even 25 times as much time.

For this reason and because the fractal structure only exists at smaller
lengthscales we have taken only a part of the total system. In fact, we have
taken at random a part of the system, which appeared to consist of 1011
discs. This new structure has been plot in figure 10.2 on the left hand side.
As can be seen, this structure is not as regular as a Vicsek fractal, because
of which we also expect a smoother slope in the diffraction spectrum. This
spectrum is shown in the same figure on the right hand side. Indeed the
slopes of respectively the fractal dimension of the aggregate and the discs
can be seen in this spectrum as well as the transition range.

Figure 10.2: A fractal aggregate built of discs (left) and its diffraction spec­
trum as calculated with ParStruc (right).
Chapter 11

General conclusions

Just like the total report, the conclusions can be divided in two parts. The first part deals with the analytical model which we have derived, whereas the other part has relation with the data the model has been applied to.

In the first place, we have developed a new analytical model for small-angle X-ray scattering spectra. Earlier studies have been performed on this topic, even in the area of asphaltenes. However, this new analytical model distinguishes itself essentially from the earlier studies by using a completely new approach. In fact, whereas the former studies were all based on the principle of Debye, we have substituted a multipole expansion in the basic formula. In this way, we have developed a model which contains:

- The shape of the particles and aggregates (e.g. sphere, disc),
- The ordering of the particles (e.g. uniform distribution, orientation correlation, fractal structure) and
- Polydispersion in particle or aggregate size.

This new analytical tool is especially powerful in combination with the computer program PARSTRUC, which calculates spectra numerically. In fact, they are complementary tools since both have their advantages and disadvantages. The advantage of the analytical model is that it gives more insight in the reason why the spectrum shows like it does, but on the other hand, it has been derived for simplified configurations. The advantage of PARSTRUC is just its flexibility as a result of which the spectrum of all kind of exotic structures can be simulated. Its disadvantages are on the one hand that it costs a lot of time to translate a certain structure into an input file and to subsequently calculate the spectrum, and on the other hand that such spectrum does not give much insight unless one calculates a lot of these for slightly different structures.

The second part of this report deals with the application of the model to experimental data. Several aspects of the structure can be determined easily by looking at the diffraction spectrum. However, some characteristics in a spectrum can arise because of different reasons. For example, there are three possible reasons for the appearance of a slope in the spectrum. As
a result, the structure cannot be determined as a simple inversion of the
spectrum, but all possibilities have to be considered.

First, the data available in the literature have been studied, but it
turned out that there are scarce data available which have been measured on
residues and which are also plotted on a log-log scale. Thus, to qualitatively
fit our model, we have mainly evaluated in-house (Shell) small-angle X-ray
scattering data on residues.

The application of our model to these experimental in-house data has
given us information about the structure of the asphaltenes. Most striking
is that the structures of different residues at room temperature appear to
have a lot of resemblance. In fact, these structures consist of stacks of discs
which in turn can aggregate. About these aggregates can be said that an
increasing thermodynamical instability of the residue appears to coincide
with an increasing fractal range in the aggregate part of the diffraction
spectra. However, deviating structures, for example higher stacks, may exist,
e.g. in residues from crudes of totally different regional origin.
Bibliography


Appendix A

ParStruc

In this report we derive the diffraction spectra of some configurations analytically. This may yield useable formulas for the diffraction spectrum in case these configurations have a special geometry, but in a lot of cases the diffraction spectrum can only be determined numerically.

In order to obtain diffraction spectra by numerical computation, some computer programs exist, for instance DALAI, an in Fortan implemented program developed at the Eindhoven University of Technology, and PARSTRUC [7], a parallel program developed at the Shell Research and Technology Centre Amsterdam. Both programs are based on the Debye scattering formula. We have used PARSTRUC, since the advantage of PARSTRUC is its parallel design which offers the possibility to execute the program fast on parallel networks.

The structures have to be built of atoms. This is in contrast with our analytical model where we assume a homogeneous distribution within a particle of a certain shape. This has been illustrated in figure A.1 where two discs have been plotted, respectively as used by PARSTRUC and as used by our analytical model.

![Figure A.1: A disc respectively as used by ParStruc (left) and as used by our analytical model (right).](image)

The speed of the parallel program can be useful for large systems since the total number of calculations to be performed to compute the function of Debye is quadratically dependent on the number of particles. Namely, for structures built of individual scatterers, typically non-penetrating spheres,
the formula of Debye (1915) can be employed

\[ I(q) = \sum_{j=1}^{N} \sum_{k=1}^{N} f_j(q)f_k(q) \frac{\sin(qr_{j,k})}{qr_{j,k}}, \]  

(A.1)

where \( N \) is the number of particles in the aggregate, \( r_{j,k} \) is the pair distance of particle \( j \) and \( k \), \( q \) is the scattering vector and \( f_j(q) \) is the atomic scattering factor (form factor) of the \( j \)th atom. This form factor expresses the scattering behaviour of the individual atoms.