Structure and fluorescence of photonic colloidal crystals

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X-ray scattering of colloidal spheres

8.1 Introduction

Knowledge of the size and internal structure of the particles in a colloidal crystal is of critical importance for photonic applications; for example, the density profile inside the spheres is directly related to the refractive index, which determines the photonic band structure. A thorough understanding of scattering from individual particles is essential for the interpretation of diffraction patterns from groups of particles, e.g. colloidal crystals. Surprisingly, the internal structure of colloidal particles is seldom investigated.

Here we present a synchrotron small-angle x-ray scattering study of colloidal particles that are widely used, namely polystyrene latex and two types of silica spheres. Although the use of x-ray scattering for characterizing colloids has been known already since the early 1950s, it does not seem to have found widespread application, in spite of the fact that the technique has several major advantages: it probes a wide range of length scales, it allows us to probe inside the particles, the method is in situ, and it does not suffer from multiple scattering.

The potentials of small-angle x-ray scattering have been demonstrated by Ballauff et al. and in the use of ultra-small angle scattering by e.g. Dosho et al. Recently, x-ray scattering is rejoicing in a growing interest, stimulated by results such as those presented here. Surprisingly, synchrotron sources have hardly been used until a few years ago, in spite of pioneering work by Sirota et al. and Chang et al. Modern synchrotron sources are ideally suited for small-angle scattering. These sources have a high brilliance, so the acquisition time can be short (fractions of a second); they deliver a highly monochromatic beam which is tightly collimated and has a narrow focus, so the angular resolution is high. In combination with the high dynamic range of the detector, this makes synchrotron small-angle x-ray scattering an ideal tool for the study of colloidal systems.
8.2 Experiments

We have studied several different kinds of colloidal particles of various radii. Silica spheres were grown by Stöber synthesis or by polymerization in a microemulsion, and were kindly provided by A. van Blaaderen and A. Imhof. Polystyrene colloids were obtained from Duke Scientific or kindly provided by J. Verhoeven. Table 8.3 at the end of this chapter summarizes the names and origins of the various colloidal systems. The particles were suspended in various solvents (water, methanol, ethanol, or dimethylformamide) by successively diluting and centrifuging. The final volume fraction of the diluted suspensions was usually 0.1% or less to prevent effects from particle interactions.

The colloidal suspensions were sealed in glass capillaries. For this purpose we employed 2 mm diameter round capillaries with 0.01 mm thin walls (Hilgenberg) and flat capillaries with a 0.3 or 0.4 mm inside path length and 0.3 mm thick walls (Vitro Dynamics). Because colloidal crystals usually have their close-packed planes parallel to the walls of the capillary, it is advantageous to use flat capillaries. Therefore we have also tried to measure diffraction patterns from dilute suspensions in the flat, thick-walled capillaries, but this resulted in a much higher background. Most of the results that we present derive from diffraction patterns taken with thin-walled capillaries.

8.3 Particle radii

Figure 8.1 shows the experimentally determined scattering cross section as a function of scattering vector $s$ for dilute suspensions of the different kinds of particles studied: polystyrene, Stöber grown silica, and microemulsion-grown silica spheres. The cross sections vary over more than 5 orders of magnitude. For weakly scattered radiation like x-rays, the amplitude of the scattered radiation is the coherent sum of contributions from different parts of a particle (Rayleigh-Gans scattering). The intensity of the scattered radiation has its maximum in the forward direction ($s = 0$) where all contributions are in phase. Away from the forward direction the cross section gradually decreases because contributions from different parts of the sphere start to interfere destructively. The interference gives rise to fringes in the cross section as a function of $s$, that are clearly illustrated in Fig. 8.1. The radius $r$ of the spheres can be determined with high accuracy, and in situ, from the positions of the fringes. The presence of a large number of fringes indicates that the spheres are nearly monodisperse, because even a moderate (~ 10%) size polydispersity (standard deviation of the radius divided by the mean) almost completely washes out the fringes.
Figure 8.1  Scattering cross section $I_0$ as a function of scattering vector $s = 2\sin(\theta)/\lambda$ for dilute suspensions of spheres, plotted semilogarithmically (left panels) or on a linear scale and multiplied by $s^4$ (Porod plot, right panels): (a) polystyrene in methanol (polystyrene-1); (b) microemulsion-grown silica in dimethylformamide (microemulsion-2); (c) Stöber grown silica in water (silica-2). The solid lines are model curves for spheres of homogeneous internal density, taking into account size polydispersity and detector blurring. The presence of a large number of fringes indicates that the sizes of the spheres are highly monodisperse. The polydispersity can be determined from the fringe amplitude (arrow) as a function of $s$. If the scattering cross section is multiplied by $(2/9)(2\pi r)^4$ instead of $s^4$, then the average height of the fringes ($\cdots$) yields the cross section in the forward direction ($s = 0$). This cross section can also be obtained from the Guinier plots (inset). The dotted lines with a slope of $(2\pi r)^2/5$ in the Guinier plots have been drawn using the radii deduced from the fringe period.
To gain a further understanding of the particle shape, we consider the exact expres­sion for the differential scattering cross section of a single homogeneous sphere of radius \( r \) with a sharp edge\(^{5,11,22} \)

\[
I(s) = I_e N_e^2 \Phi^2 (2\pi sr).
\]  

(8.1)

Here \( I_e \) is the cross section for a single electron (a constant), \( r \) is the radius of the sphere. \( N_e = (4/3)\pi r^3 \Delta n_e \) is the number of excess electrons in the sphere with respect to the surroundings, and \( \Delta n_e \) is the difference in electron density. The angular dependence of the cross section is determined by the spherical Bessel function \( j_1(x) \)

\[
\Phi(x) = 3 \frac{j_1(x) - x \cos(x)}{x^3}.
\]

(8.2)

Beyond the first fringe \( (x > \pi) \), the square of the Bessel function decreases as \([1 + \cos(2x)]/x^4\). The fourth power of \( s \) causes the variation of \( I \) over 5 orders of magnitude in Fig. 8.1. The radius and polydispersity can be conveniently obtained by presenting the data in a Porod plot (Fig. 8.1), i.e. multiplied by \( s^4 \) and on a linear scale. For perfect spheres the resulting curves should go like \( \cos(4\pi sr) \) at large \( rs \). The experimental curves indeed look like a sine, but the oscillations gradually decrease with increasing \( s \), as a consequence of the polydispersity of the spheres. The positions of the minima and maxima in the Porod plot are determined by the average sphere radius and hardly affected by a small polydispersity. Hence, the radius of the spheres can be very accurately determined by plotting the positions of the minima and maxima. The resulting plot for the polystyrene spheres is shown in Fig. 8.2. The slope of the line corresponds to half the inverse radius. We have obtained a radius of the spheres in suspension of \( r = 100.9 \pm 0.5 \text{ nm} \), close to the radius specified by the manufacturer, \( r = 99 \text{ nm} \). The statistical errors in the radii thus determined are on the order of only 0.5 \%, which clearly illustrates the potential of the method.

We have obtained radii for many colloidal systems of nearly monodisperse spheres. The nature of the various systems, along with radii determined by x-ray scattering and other methods, and the polydispersities are summarized in table 8.1. For some colloids we have measured the radius in several solvents. The radii were identical within experimental uncertainty,\(^{23} \) which indicates that the spheres do not swell in the liquids that we have used. The radii determined by x-ray scattering for the polystyrene systems are in excellent agreement with the radii specified by Duke Scientific. The radii obtained by static light scattering also closely correspond, as expected because light scattering and x-ray scattering are basically the same techni­ques.\(^{21} \) We take the excellent agreement as a validation of the x-ray technique. The radii determined by transmission electron microscopy are systematically on the
order of 10% lower than the other results, probably because the particles are dried so they shrink, and the electrons sometimes degrade the material. There is a considerable variation in these radii. One would expect that radii can be determined with high accuracy using electron microscopy, because it is possible to determine quite small polydispersionsities (down to a few percent) with this technique. The variation suggests that different colloidal systems shrink by different amounts. Radii determined by dynamic light scattering, based on measuring Doppler shifts due to Brownian motion of the particles, tend to be higher than the radii determined by the other methods. This has been observed previously; possibly the spheres drag some extra liquid along with them, for instance due to interactions with counterions which are in solution. Furthermore, there is a considerable variation in the data, on the order of 10%. It has been shown previously that dynamic light scattering is rather sensitive to the presence of surfactants, salts, and the volume fraction of the colloid, which may explain the variation in the radii. However, if one makes ev-

Figure 8.2  Positions of the minima and maxima in the Porod plot (Fig. 8.1a) versus the order of the minimum (n) or maximum (n + 1/2). The slope of the fit (—) yields the radius, \( r = 100.9 \pm 0.5 \) nm, in excellent agreement with the value specified by the manufacturer, 99 nm. The lower panel shows the small difference between the datapoints and the fit in the upper panel. Note that the simple straight line is not expected to accurately predict the position of the first maximum (leftmost data point).
every effort it is possible to determine very accurate radii using dynamic light scattering. This is clearly demonstrated by the excellent agreement between x-ray radii and the results of Duke Scientific, which were obtained by dynamic light scattering.

8.4 Size polydispersity

For monodisperse spheres, the curves in Fig. 8.1 should go like \(1 + \cos(4\pi rs)\) at large \(rs\), but the amplitude of the observed modulations decreases with increasing \(s\) as a consequence of the polydispersity of the spheres. The form factors of spheres with different radii are identical, but the horizontal scale is different. The scattered intensities of individual spheres add, but with the fringes shifted, so the fringes average out. The fringes at high \(s\) are shifted more (in the absolute sense), so they average out more easily. Thus the decrease of the fringe amplitude is a measure of the polydispersity.

If the polydispersity is small, the distribution of radii closely resembles a Gaussian. For a Gaussian distribution, the average cross section can be calculated analytically if we assume that the electron density is the same for all spheres. It appears that the oscillating terms in \(\Phi^2\) decrease with a factor \(\exp[-2(2\pi rs\delta)^2]\), where \(\delta\) is the polydispersity, \(i.e.\) the standard deviation of the radius divided by the mean. This is a very useful result, because it provides a straightforward method to determine the polydispersity from the amplitudes of the fringes in a Porod plot, as we will demonstrate below. The method that we present here is both quantitative and convenient, as it eliminates the need for elaborate fitting procedures.

In Fig. 8.3 we have plotted the amplitude of the fringes in Fig. 8.1 as a function of \((rs)^2\). Such a semilogarithmic plot should give a straight line, except at low \(s\), near the first maximum in the Porod plot. Indeed the fringe amplitudes in Fig. 8.3 agree with a straight line. From the slope of the line we find a polydispersity \(\delta = \Delta r / r = 2.3 \pm 0.3\%\), excellent agreement with the polydispersity specified by Duke Scientific, \(\delta = 2.1\%\). It shows that x-ray scattering is well suited to accurately determine small polydispersities (below 5%). We stress that our characterization of the particle size distribution is an \textit{in situ} technique, as opposed to techniques that are normally used, such as transmission electron microscopy.

There are several experimental effects which may also affect the amplitude of the fringes in Fig. 8.1, namely the polychromaticity of the x-rays, the finite focus spot size, the beam divergence and the finite detector resolution. Only polychromaticity has the same influence as a polydispersity of the spheres. Fortunately, the relative spectral width of the source is approximately \(1.5 \times 10^{-4}\), which is completely negligible compared to polydispersions of colloidal dispersions (> \(10^{-2}\)). For comparison, in small-angle neutron scattering the relative spectral width is of-
Thin walled capillaries; wavelength \( \lambda = 0.14725 \text{ nm} \)

<table>
<thead>
<tr>
<th>System</th>
<th>( r_{\text{TEM}} )</th>
<th>( r_{\text{SAXS}} )</th>
<th>( r_{\text{SLS}} )</th>
<th>( r_{\text{DLS}} )</th>
<th>( \delta_{\text{TEM}} )</th>
<th>( \delta_{\text{SAXS}} )</th>
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<tr>
<td>polystyrene-1</td>
<td>100.9(5) (^b)</td>
<td>99(^f)</td>
<td>2.1(^f)</td>
<td>2.3(3)</td>
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<td></td>
</tr>
<tr>
<td>silica-1</td>
<td>114</td>
<td>138(3)(^c)(^d)</td>
<td>148(7)</td>
<td>161</td>
<td>3.6</td>
<td>3.05(5)</td>
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<tr>
<td>silica-2</td>
<td>156</td>
<td>178.5(7)(^c)(^d)</td>
<td>178(5)</td>
<td>216</td>
<td>3.6</td>
<td>2.9(1)</td>
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<tr>
<td>silica-2</td>
<td>184.0(4)(^e)</td>
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<tr>
<td>silica-4</td>
<td>89.4</td>
<td>94.9(1.6)(^d)</td>
<td>107.2(3)</td>
<td>2.1/3</td>
<td>6</td>
<td>5.5(2)</td>
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<tr>
<td>silica-5</td>
<td>179</td>
<td>199.0(1.8)(^d)</td>
<td>200(3)</td>
<td>188(5)</td>
<td>5.5</td>
<td>4.4(3)</td>
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<tr>
<td>silica-6</td>
<td>187</td>
<td>211.4(5)(^e)</td>
<td>211(1)</td>
<td>213(3)</td>
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<td>microemulsion-1</td>
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<td>1.3(1)</td>
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<td>28.0(5)(^f)</td>
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<td>1.5</td>
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<td>26.3(5)(^c)</td>
<td></td>
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</table>

Thick walled capillaries; wavelength \( \lambda = 0.09880 \text{ nm} \)

<table>
<thead>
<tr>
<th>System</th>
<th>( r_{\text{TEM}} )</th>
<th>( r_{\text{SAXS}} )</th>
<th>( r_{\text{SLS}} )</th>
<th>( r_{\text{DLS}} )</th>
<th>( \delta_{\text{TEM}} )</th>
<th>( \delta_{\text{SAXS}} )</th>
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<tr>
<td>polystyrene-2</td>
<td>102.0(3)(^h)(^e)</td>
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<td></td>
<td></td>
<td>101.5(^f)</td>
<td>2.1(^f)</td>
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<tr>
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<td></td>
<td></td>
<td>111(^f)</td>
<td>2.0(^f)</td>
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<td>polystyrene-4</td>
<td>120.8(5)(^e)</td>
<td></td>
<td></td>
<td></td>
<td>120.5(^f)</td>
<td>1.6(^f)</td>
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<tr>
<td>polystyrene-5</td>
<td>198.5(^g)</td>
<td>200.6(5)(^e)</td>
<td></td>
<td></td>
<td>211.5</td>
<td></td>
</tr>
<tr>
<td>silica-1(^a)</td>
<td>114</td>
<td>144(2)(^e)</td>
<td>148(7)</td>
<td>161</td>
<td></td>
<td></td>
</tr>
<tr>
<td>silica-2</td>
<td>156</td>
<td>185.5(1.3)(^e)</td>
<td>178(5)</td>
<td>216</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>silica-3</td>
<td>208</td>
<td>248.4(1.1)(^e)</td>
<td>241(7)</td>
<td>260</td>
<td></td>
<td></td>
</tr>
<tr>
<td>microemulsion-2</td>
<td>25.7</td>
<td>27.8(4)(^c)</td>
<td></td>
<td></td>
<td></td>
<td>1.5</td>
</tr>
<tr>
<td>microemulsion-3</td>
<td>26.7(5)(^c)</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

\(^a\)These spheres consist of a core of \(101 \pm 2 \text{ nm} \) and a \(37 \pm 2 \text{ nm} \) thick shell of lower density. 
\(^b\)In methanol; \(^c\)In dimethylformamide; \(^d\)In water; \(^e\)In ethanol. 
\(^f\)Specified by Duke Scientific; \(^g\)SEM instead of TEM.

Table 8.1 Radii \( r \) (in nanometers) and polydispersities \( \delta \) (in percent) for a number of colloidal systems, obtained by transmission electron microscopy (TEM), small-angle x-ray scattering (SAXS), static light scattering (SLS), or dynamic light scattering (DLS).
ten of the order of 0.1; hence this completely dominates the polydispersity of the spheres. The other effects, i.e. the focus size at the sample, the beam divergence, and the finite detector resolution, all affect the fringes in the following way: the measured diffraction pattern is equal to the ideal pattern, convoluted with the profile of the direct beam. This convolution corresponds to small shifts of the diffraction pattern; because all fringes shift by equal amounts, they are all affected equally. It appears that due to these effects the fringe amplitude decreases by a factor which is independent of $s$. Thus it is possible to separate the influence of polydispersity and the instrument response, because the dependences on $s$ of the effects are different. The abscissa of the line in Fig. 8.3 is a measure of the r.m.s. width $\Delta$ of the beam profile. We find $\Delta = 0.72 \pm 0.10$ mm. This is in reasonable agreement with the experimentally determined width of the direct beam on the detector, which is $\Delta = 0.60$ mm (horizontally) and 0.38 mm (vertically).

The polydispersities for several dilute colloidal systems of nearly monodisperse spheres have been determined using small-angle x-ray scattering, see table 8.1. The ratio of polydispersities determined by electron microscopy and by x-ray scattering is plotted in Fig. 8.4. For comparison, we have also included the polydispersity from dynamic light scattering discussed above. The polydispersities from electron microscopy are consistently larger than the corresponding polydispersities from x-ray scattering. The discrepancy gradually becomes larger with decreasing $s$.

![Figure 8.3](image)

Figure 8.3  Amplitude of the fringes in Fig. 8.1a, normalized to the average height, as a function of $(rs)^2$. The fringe amplitude decreases as $\exp[-2(2\pi rs)^2]$, which is a straight line in this plot. The slope of the fit ($\cdots$) yields the polydispersity, $\delta = 2.3 \pm 0.3\%$, in excellent agreement with the polydispersity specified by the manufacturer, $\delta = 2.1\%$. 

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polydispersity. This can be explained from the method to determine polydispersions by electron microscopy. These polydispersions are determined by measuring the diameters of a large number of particles on a grid and calculating the variance. The polydispersity is then computed as the root of the variance (i.e., the standard deviation) divided by the mean diameter. However, the variance of the measured diameters is not equal to the variance of the distribution of diameters but also includes an additional contribution due to the random error in the determination of the diameters of the individual spheres. Because the magnification of the microscope is usually adjusted according to the size of the particles, one would expect the absolute error to be proportional to the particle size. The resulting observed polydispersity is then $\delta_{\text{obs}} = \sqrt{\delta_{\text{true}}^2 + \delta_{\text{err}}^2}$, where $\delta_{\text{true}}$ is the true polydispersity of the particles and $\delta_{\text{err}}$ is the uncertainty in a measurement divided by the particle size. We have calculated this $\delta_{\text{obs}}$ assuming that the x-ray polydispersity is correct and for a relative random error $\delta_{\text{err}}$ in the observed radii of 2 and 3%. The resulting polydispersity ratios are plotted in Fig. 8.4. The agreement with the experimentally observed ratio is striking. Hence we conclude that the small polydispersities determined by electron microscopy are probably too high; i.e., they are rather an upper bound for the true polydispersity of the particles.
8.5 Particle-medium interface

Measuring the scattering cross section out to large scattering vector $s$, i.e. more than just one fringe, in principle yields information at small length scales. Some details have a pronounced effect on the diffraction pattern, even if the deviation from a perfect sphere of homogeneous density is small, for instance the presence of a smooth edge instead of a sharp one. So far we have assumed that the particles have a sharp edge, i.e. that the electron density abruptly changes at the interface to the medium. A smooth interface reveals itself immediately in the scattering cross section, as can be readily shown using the convolution theorem. The electron density of a particle with a smooth interface region can be constructed mathematically as the convolution of the electron density of a particle with a sharp edge and a smooth function which describes the blurring at the edge. The corresponding scattering cross section is the cross section of the particle with a sharp edge multiplied by the squared Fourier transform of the blurring function. If we take a Gaussian with a small width for the blurring function, then the cross section is multiplied by a broad Gaussian, so it starts to decrease faster than $s^{-4}$ at high $s$. In a Porod plot like Fig. 8.1, spheres with a sharp edge would show a function which oscillates around a constant value, while the function would gradually decrease at high $s$ if the edge were smooth. Note that the decrease affects the cross section as a whole, not just the oscillating terms as with polydispersity, so the effects of a smooth edge and polydispersity can be separated.

Since the Porod cross section in Fig. 8.1 oscillates around a constant value, we conclude that the edges of these spheres are rather sharp. Considering the average Porod cross section of the polystyrene spheres to be constant to within a fraction $\varepsilon = 10\%$ over the whole range of $s$ in the figure, we estimate the width $\sigma$ of the interface-blurring Gaussian in reciprocal space from $[\exp(-s^2/2\sigma^2)]^2 = 1 - \varepsilon$. Taking $s = 5 \times 10^{-2}$ nm$^{-1}$, the upper bound for the thickness of the edge is $1/(2\pi\sigma) = 1.0$ nm, so the density indeed changes abruptly at the edge of the polystyrene spheres. Similar values are obtained for Stöber-synthesized silica. For silica surfaces, the edge layer has been reported$^{31}$ to have a thickness of $1 - 2$ nm, in agreement with our result. The method just described could be a valuable means of studying the phase separation of a mixture of two liquids at the surface of colloidal particles. The preferential adsorption of one of the fluids on the surface near the critical point of wetting is of fundamental importance.$^{32}$
8.6 Electron Density

The forward scattering cross section \( I(s \to 0) \) is related to the difference in electron density of the medium and of the particles, \( \Delta n_e \), and the size and number of spheres in the scattering volume.\(^{11}\) We can estimate the volume fraction \( \varphi \) of spheres in the liquid from the cross section per unit volume \( I_v \) using

\[
\varphi = \frac{3}{\Delta n_e^2 4\pi r^3} \frac{1}{r_v^2} I_v. \tag{8.3}
\]

The electron densities can be estimated from the number of atomic masses per proton \( M/Z \) and the mass density \( \rho \). The densities for relevant materials are listed in table 8.2. The radius is determined with high accuracy from the positions of the minima and maxima in the Porod plot, see Fig. 8.2. However, it is difficult to measure the forward scattering cross section because of the presence of the unscattered beam.

To estimate the forward cross section, the experimental cross section is extrapolated to \( s = 0 \) using a Guinier plot, as shown in the insets of Fig. 8.1. The slope of \( (2\pi r)^2/5 \) in the Guinier approximation is determined by the radii estimated from the fringes, \( cf. \) table 8.1. The inset of Fig. 8.1a reveals an excellent agreement between the data and the Guinier approximation. The excellent agreement also demonstrates that there are no saturation effects of the detector. Saturation effects usually occur near the beam stop and would reveal a decrease at small \( s \) and a deviation from the straight line. For the microemulsion-grown silica (Fig. 8.1b) the Guinier slope is also in good agreement with the data, except for a small deviation at small \( s \). This is possibly due to a small number of coagulated spheres ("dumbbells") that occur in microemulsion-grown dispersions\(^{16}\) and that were detected by TEM. These composite particles are larger; hence, they give rise to scattering at low \( s \). Furthermore the cross section of these particles is larger, proportional to the volume of the particle, which explains why a small number of them is detectable. In Fig. 8.1c, the Guinier slope is in moderate agreement with the data. We have no explanation for the not so good agreement in Fig. 8.1c in comparison with Figures 8.1a and 8.1b.

The forward scattering cross section can also be derived from the Porod plot, as a check. The average height of the fringes in a Porod plot should correspond to the scattering cross section extrapolated to \( s = 0 \) in the semilogarithmic plots of Fig. 8.1. The data on polystyrene spheres in this figure give a forward scattering cross section of \( 8.2 \times 10^5 \text{ sr}^{-1}\text{m}^{-1} \), in good agreement with the Guinier estimate of \( 7.5 \pm 0.4 \times 10^5 \text{ sr}^{-1}\text{m}^{-1} \). However, the calibration of the absolute intensities was probably incorrect during the first run, and this affects the measured cross sections. In a later run we have repeated our measurements on the polystyrene colloids in ethanol, paying due attention to the determination of absolute intensities. We have
prepared suspensions with volume fractions of 0.1%. From the forward scattering cross section we derived a difference in electron density of polystyrene and ethanol of 66, 89, and 67 nm$^{-3}$ respectively, in excellent agreement with the expected value of $66 \pm 8$ nm$^{-3}$, cf. table 8.2. This shows that absolute intensities can be measured accurately.

The scattering cross section of polystyrene-water systems is very low, because the electron density of the most common solvent, water, is very closely matched to that of polystyrene. The weak scattering of this ubiquitous colloidal system may well be a reason why there have been so few reports on small-angle x-ray scattering and colloids. For the polystyrene-3 spheres in water we have determined the forward scattering cross section to be less than $1.5 \times 10^3$ sr$^{-1}$ m$^{-1}$ at a volume fraction $\phi$ of 0.1%, which corresponds to a difference in electron density of the polystyrene spheres and water of less than 2%. The associated mass density of the colloidal polystyrene is $1.03 \pm 0.02$ g cm$^{-3}$, in good agreement with the density quoted by Duke Scientific, 1.05 g cm$^{-3}$.

Knowing the cross section in the forward direction, the radius, and the polydispersity, it is possible to calculate the complete scattering cross section as a function of $s$. These theoretical cross sections are shown as solid curves in Fig. 8.1. The width of the detector profile is taken into account. The agreement with the experimentally observed cross sections is very good, especially for the polystyrene system, where it extends over more than 5 orders of magnitude. Only for the microemulsion-grown silica there are some small discrepancies, possibly caused by the presence of “dumbbells”. We conclude that the cross sections of both polystyrene and Stöber silica systems are completely consistent with those of homogeneous, nearly monodisperse spheres with a sharp edge. Such a comparison of experimental and theoretical cross sections is quite a severe test, as will be demonstrated in the next section.

Table 8.2  Electron densities $n_e$ of relevant colloidal materials and suspending liquids, estimated from the atomic mass per proton $M/Z$ and the mass density $\rho$.

<table>
<thead>
<tr>
<th>Material</th>
<th>Structure</th>
<th>$M/Z$</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>$n_e$ (e$^-$/nm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>CH$_3$OH</td>
<td>1.78</td>
<td>0.81</td>
<td>272</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C$_2$H$_5$OH</td>
<td>1.77</td>
<td>0.79</td>
<td>267</td>
</tr>
<tr>
<td>Dimethylformamide</td>
<td>C$_3$H$_7$NO</td>
<td>1.83</td>
<td>0.95</td>
<td>311</td>
</tr>
<tr>
<td>Polystyrene latex</td>
<td>C$_8$H$_8$</td>
<td>1.86</td>
<td>1.00-1.05</td>
<td>322-338</td>
</tr>
<tr>
<td>Water</td>
<td>H$_2$O</td>
<td>1.80</td>
<td>1.00</td>
<td>333</td>
</tr>
<tr>
<td>Silica (colloidal)</td>
<td>SiO$_2$</td>
<td>2.00</td>
<td>1.9-2.0$^{13,17,34}$</td>
<td>570-600</td>
</tr>
</tbody>
</table>
8.7 Internal structure

An attractive capability of x-ray scattering is the ability to examine the density profile in the spheres, e.g. to see whether the spheres consist of shells of different density. In such situations one traditionally resorts to contrast matching with a suitable suspension liquid,\textsuperscript{1} which is indispensable for detecting small density differences. Here, we show that it is in some cases possible to detect inhomogeneities even without matching. This is probably due to a considerable density difference.

As an illustration, the Porod cross section of a dilute suspension of silica-1 spheres is shown in Fig. 8.5. These spheres have had no special treatment, but the cross section is totally different from the cross sections of the other spheres, cf. Fig. 8.1. Similar silica systems (for instance silica-2) give scattering patterns in accordance with that of homogeneous spheres, so there is something peculiar only with the silica-1 system. As a check, we measured diffraction patterns for the same silica-1 spheres in different liquids and at several different volume fractions, but the cross sections appeared identical.

Silica spheres are often synthesized in steps, growing additional layers of sil-
ica on smaller particles until the desired diameter is reached. A density difference between the core and the additional layers would show up as an extra oscillation, as in Fig. 8.5. The scattering cross section of a core-and-shell sphere can be easily calculated using the result for a homogeneous sphere (Eqs. 8.1 and 8.2): the excess electron density of the core-with-a-shell sphere can be made up of two homogeneous spheres with different radii and densities,

\[ I_{\text{core-shell}} = I_e N_e^2 \left[ (1 - v)\Phi(x) + v(1 + b)^3\Phi((1 + b)x) \right]^2, \]  

(8.4)

where \( x = 2\pi r s \) with \( r \) the radius of the core, \( d \) is the thickness of the shell, \( b = d/r \) is the thickness of the shell as a fraction of the core radius, \( N_e \) is the number of excess electrons in the core, and \( v \) is the electron density difference between the shell and the liquid as a fraction of the core excess electron density difference.

We have plotted the cross section for such a core-and-shell sphere in Fig. 8.5, taking into account polydispersities for the core radius and shell thickness, their correlation, and the blurring due to the finite resolving power of the instrument. The calculated curve represents the observed scattering cross section reasonably well, although there are some discrepancies at small and large \( s \). These may be caused by additional shells or density gradients in the spheres.

The calculated scattering cross section corresponds to spheres with a core radius \( r \) of \( 101 \pm 2 \) nm and a shell thickness \( d \) of \( 37 \pm 2 \) nm, in good agreement with radii measured by static light scattering before and after the last synthesis step, \( 101 \pm 7 \) and \( 148 \pm 7 \) nm. From the relative electron density difference \( v = 81 \pm 3\% \) and the electron densities of water and silica in Table 8.2 we estimate that the shell has an \( 8 \pm 2\% \) lower mass density than the core. This is a sizeable difference in density, considering that the layers were grown using the same synthesis method. On the other hand, there is a comparable variation in the experimentally determined densities of colloidal silica. \(^{13,17,33,34} \)

### 8.8 Conclusions

We have shown that the technique of synchrotron small-angle x-ray scattering is very well suited for the characterization of colloidal spheres. The size of colloidal spheres can be determined \textit{in situ} and with high accuracy. We have determined the radii of many different kinds of colloidal spheres from the positions of the minima and maxima of the differential scattering cross section as a function of wavevector. The radii are in excellent agreement with those determined by static light scattering. Electron microscopy consistently yields radii that are smaller and dynamic light scattering yields radii that are larger than the radii determined by x-ray scattering.
We have presented a straightforward method to deduce the size polydispersity of nearly monodisperse (polydispersity < 10%) spheres from a Porod plot of the differential scattering cross section, thus eliminating the need for elaborate fitting procedures. A comparison with polydispersions determined by electron microscopy shows that the new method makes it possible to accurately determine even very small polydispersions (~ 2%). Our data suggest that polydispersions determined by electron microscopy are an upper bound to real polydispersities.

We have shown that it is possible to study details of the spheres, for instance the sharpness of the outer edge of the spheres. The thickness of the edge of polystyrene spheres of 100 nm radius was estimated to be less than 1 nm. Similar thicknesses are observed for silica spheres, in agreement with observations on silica surfaces. Thus, picturing polystyrene and silica spheres as objects with an abrupt edge is justified.

A Guinier plot was used to determine the forward scattering cross section, which in turn yields the volume fraction or the excess electron density of the spheres. The excess electron densities of several systems including the closely matched system polystyrene and water were obtained, in good agreement with literature data.

Using our data, we have calculated the scattering cross section as a function of wavevector, assuming that the spheres are homogeneous and that they have a sharp edge. The agreement of the calculated curves with the experimentally observed cross sections is excellent, especially for the polystyrene system where it extends over 5 orders of magnitude.

As an example of a more complicated system, we have discussed a suspension of silica spheres which show a peculiar modulation in the cross section, caused by an inhomogeneous intraparticle density. The qualitative features of the cross section were captured by supposing that the spheres consist of a core surrounded by a shell of less dense material. This is a reasonable assumption because the spheres were synthesized by growing additional silica layers on smaller particles. The core radius is in agreement with the size determined before the last synthesis step using static light scattering. The core radius, the shell thickness, and the ratio of the density of core and shell could be obtained even without contrast matching with the suspension liquid, i.e., in situ.

References

6. Traditionally, colloidal systems are studied with small-angle neutron scattering.\(^1\) Science Abstracts 1995 yields only 9 references when searched for the keywords “SAXS” and “colloid”, while for “SANS” and “colloid” there are over 50 references.


20. The high background prevented an accurate determination of the polydispersity of the samples in the thick-walled capillaries. The background is especially bothersome at large \(s\). As a result, the obtained scattering patterns are different from those obtained with thin-walled capillaries and do not decrease as \(s^{-4}\), but more slowly.


23. One exception is the silica system SC200, which appears to be 3% larger in ethanol than in water or dimethylformamide. The radius of the SC200 system in ethanol was reproduced in two different runs. We have no explanation for this difference.


26. This polydispersity includes a contribution due to a possible ellipticity of the particles, because the form factor for an ellipsoid is identical to that of a sphere with an effective radius which varies between the smallest and largest radii of the ellipsoid depending on its orientation.\textsuperscript{21}


28. The first fringe is expected to be a little bit higher, because the first fringe in a Porod plot of the form factor of a perfect sphere is also higher than the other fringes.


30. The error bars of the polydispersity ratios is based on a relative error in the polydispersities determined by electron microscopy of 10%. The theoretical relative error in this polydispersity is $1/\sqrt{2k-2}$, where $k$ is the number of particle diameters measured; for $k = 50$ the relative uncertainty is $\sim 10\%$. The situation improves only slowly with particle number.


Table 8.3 Key to the sample designations used in the text.

<table>
<thead>
<tr>
<th>System</th>
<th>Original name</th>
<th>Source</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>polystyrene-1</td>
<td>PS5020A</td>
<td>Duke Scientific</td>
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<tr>
<td>polystyrene-2</td>
<td>PS5020A&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Duke Scientific</td>
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</tr>
<tr>
<td>polystyrene-3</td>
<td>PS5022A</td>
<td>Duke Scientific</td>
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<tr>
<td>polystyrene-4</td>
<td>PS5024A</td>
<td>Duke Scientific</td>
<td></td>
</tr>
<tr>
<td>polystyrene-5</td>
<td>A11</td>
<td>J. Verhoeven</td>
<td>[19]</td>
</tr>
<tr>
<td>silica-1</td>
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<td>C. van Kats</td>
<td></td>
</tr>
<tr>
<td>silica-2</td>
<td>SC200</td>
<td>C. van Kats</td>
<td></td>
</tr>
<tr>
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<td>SC006</td>
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<td></td>
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<tr>
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<td>silica-5</td>
<td>FSA7</td>
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<td>silica-6</td>
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<td>microemulsion-1</td>
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<sup>a</sup> This dispersion is a different batch than the other PS5020A.