A Triple-Axis Bonse–Hart Camera used for High-Resolution Small-Angle Scattering

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Abstract

A triple-axis diffractometer has been constructed and optimized in our laboratory. It is used on an X-ray point source, using the principle which was pioneered by Bonse and Hart 25 years ago. A triple-reflection channel-cut Ge crystal is used as monochromator and the same as analyser. The width of the direct beam is about FWHM = 17” for Cu Ka radiation. Owing to the low background, the stability of the mechanics and the two triple Ge reflections, a signal-to-noise ratio of $10^7$ has been achieved between the direct beam and the parasitic scattering without sample. These characteristics allow routine measurement of scattering to be performed for Bragg spacings up to 6000 Å for typical colloidal samples in semilinear collimation.

1. Introduction

Our aim is to realise measurements of the X-ray scattering of diluted colloidal solutions made with large colloidal particles. The key point in the physics of this type of colloid (latexes, clays, swollen lamellar phases, vesicles) is the knowledge of the forces between particles. These forces are usually expressed as an interaction potential whose origin may be electrostatic forces, dispersion forces or steric forces due to shape fluctuations. These forces typically range from 10 to 1000/k, which means that the relevant $q$ range ($q = 4\pi/\lambda \sin\theta$, where $\theta$ is half the scattering angle and $\lambda$ is the wavelength of the incident radiation) of the scattering lies between 0.001 and 0.01 Å$^{-1}$, i.e. for Bragg spacings between 6000 and 600 Å. With pinhole collimation, this $q$ range is usually measured only by neutron scattering (D11 at Institut Laue–Langevin, Grenoble, France) or light scattering, which has the drawback of requiring optical transparency of the sample.

We would like to make the same measurement in our laboratory with X-rays (Cu Ka radiation). Moreover, the shape of the interparticle scattering peak is important; therefore, we cannot rely on deconvolution of an experimental result, needed when the experiment is done using linear collimation. The use of a conventional SAXS camera (Huxley-Holmes or Kratky), closing the slits to very low openings, reduces the flux at the sample too much and the interaction peaks would be smeared. For monodisperse interacting particles, the scattering factorizes as $I(q) = P(q)S(q)$, where $P(q)$ is the particle form factor and the unknown $S(q)$ is the crucial “structure factor”, which is the Fourier transform of the pair correlation function between centres of particles. The thermodynamic limit of $S(q)$ at zero angle is the osmotic compressibility which diverges close to a phase transition when the colloidal solution becomes unstable. Since $P(q)$ is usually known, the aim is to measure $S(q)$ and to repeat for larger particles the methodology used for micelles and microemulsions. To the authors knowledge, reliable measurements of $S(q)$ in colloidal systems have so far only been done in point or semipoint collimation.

Our typical samples are 10% volume fractions of large particles which give a scattering which is about 100–1000 times the low-angle scattering of pure water, due to its compressibility (Levelut, 1968), which is about 100 to 1000 times less than a collagen fibre of the rat tail often used for calibration purposes.

The goal is therefore clear: design a simple camera adapted to our rotating anode, able to measure in point collimation the weak signals given at about $2\theta = 1$ mrad. The key point is the rejection ratio $R$, i.e. the ratio between the direct beam and the parasitic background at $2\theta = 1$ mrad. The rejection ratio should be at least $R = 10^6$.

2. Principle

Because the desired flux ($q > 10^6$ photons s$^{-1}$ through the sample) cannot be reduced by closing the slits and the beamstop size, we use a large source and an angular analyser. The principle of the experiment was pioneered by Bonse & Hart (1965). They used five reflections and a forecrystal in order to measure the oscillations in the form factor of an experimental result, needed when the experiment is done using linear collimation. The use of a conventional SAXS camera (Huxley-Holmes or Kratky), closing the slits to very low openings, reduces the flux at the sample too much and the interaction peaks would be smeared. For monodisperse interacting particles, the scattering factorizes as $I(q) = P(q)S(q)$, where $P(q)$ is the particle form factor and the unknown $S(q)$ is the crucial ‘structure factor’, which is the Fourier transform of the pair correlation function between centres of particles. The thermodynamic limit of $S(q)$ at zero angle is the osmotic compressibility which diverges close to a phase transition when the colloidal solution becomes unstable. Since $P(q)$ is usually known, the aim is to measure $S(q)$ and to repeat for larger particles the methodology used for micelles and microemulsions. To the authors knowledge, reliable measurements of $S(q)$ in colloidal systems have so far only been done in point or semipoint collimation.

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Because of the presence of three axes (monochromator, sample and analyser), it is very easy to change the monochromator (one, two or four reflections, Si or Ge) or to measure the X-ray reflection at the sample instead of the small-angle scattering. A fourth axis, i.e. rotating the scintillator around the analyser axis, is not used because of the small (mm) movements involved. This fourth axis is replaced by a linear displacement.

The same principle of balanced monochromators and analysers has been used on storage rings at Brookhaven National Laboratory to study smectic thermotropic and diluted lyotropic lamellar phases (Als-Nielsen et al., 1980; Roux & Safinya, 1988), at DESY in Hamburg to study supported heterogeneous catalysts (Bonse, Pahl, Nusshardt, Kinney & Pekela, 1988), at Daresbury to study muscle diffraction (Nave, Diakun & Bordas, 1986; Bordas, Mant, Diakun & Nave, 1987), at the Bartlesville Energy Research Center to study aggregation in crude oil (Dwiggins, 1978), at the Photon Factory in Japan to study the reflectivity of flat mirrors (Matsushita, Ishikawa & Kohra, 1984) and at the Philips Research Laboratories to study nearly perfect crystals (Fewster, 1988).

3. Realization

We use an RU300 rotating anode, made by Rigaku, at 18 kW with a Cu Ka target. The real source size is 1 x 10 mm, and we use the point window at 6° takeoff, which gives a source size of 1 x 1 mm full width at half-maximum (FWHM).

The triple-axis goniometer was designed and built by Microcontrole (Evry, France). Very high precision and reproducibility of the analyser and monochromator monocrystals are needed: the width of the Bragg reflection used (80 µ rad FWHM) requires a reproducibility in positioning the analyser axis better than 5 µ rad for any movement of the goniometer (χ, ψ, 0, 2θ, see Fig. 1). This cannot be achieved using a large conventional goniometer for the 2θ movement. Instead of a goniometer, we use a tangential arm and a linear encoder.

In order to keep the background intensity without sample at any q value as low as possible, the analyser crystal and detector are in vacuum. This avoids parasitic scattering in the channel of the analyser crystal as well as in the beam path between analyser and scintillator: the background is typically about 0.1 counts s⁻¹ and due mainly to the dark current of the photomultiplier used. Scintillator motors of the analyser are enclosed in a vacuum vessel. This results in a mass of about 50 kg for this ensemble rotating on the 2θ axis. To avoid any type of flexion which could perturb relative positioning of the monochromator and analyser crystals, this part of the experiment is supported by an air cushion. Unlike any conventional design using a stiff central 0,2θ axis, as in classical large goniometers, no flexion, deformation or change of crystal position after cycling could be detected using electronic levelling devices fixed at the positions of the Ge crystals.

4. Optimization

Our aim is to obtain the strongest possible flux through the sample in photons s⁻¹, with a ratio of vertical to horizontal divergence not beyond 40, in order not to smear out the interaction peaks due to repulsion between colloidal particles. The horizontal divergence of the beam at the sample is dh = 80 µ rad, set by the Ge 111 width, and is equal to the monochromator acceptance angle.

The maximum output from the monochromator would be with the shortest possible source-to-monochromator distance Dsm, around 15 cm. However, this would not allow Kα₁ and Kα₂ to be separated without using slits far from the source. Moreover, the intensity per unit solid angle in the beam coming through the monochromator is an increasing function with distance: a plateau is reached when each point of the monochromator uses each point from the source, i.e. when dhDsm > Sh, where Sh is the horizontal extension of the source. This fixes the optimal source-to-monochromator distance to be not less than 1 m with our 1 x 1 mm source. Moving toward larger distances does not increase the flux per unit solid angle of the beam and decreases the total integrated flux at fixed vertical slit opening. We usually work with 2 mm vertical slits in front of the sample, therefore the sagittal divergence of the beam is dh = 3 mrad, to be compared with...
80 μrad for the horizontal divergence. The collimation ratio at the sample is therefore \( \frac{d\nu}{dh} = 40 \). After the sample, there are no more slits except the 20 mm height of the channel. To be detected, scattering coming from the sample has to be reflected three times in the channel before being detected by the scintillator. The sample-to-scintillator distance is 600 mm. There are vertical slits in front of the analyser crystal that allow the vertical divergence to be varied after the sample. When they are open, maximum intensity from the sample is measured, at the cost of a smearing \( d\nu' = 60 \) mrad. However, for strong scatterers, \( d\nu' \) can be reduced by a factor of ten.

The optimization of the rejection ratio \( R \) and hence the final resolution relies also on the quality of the monochromators. We use a pair of three-reflection channel-cut Ge crystals which were cut, controlled for surface mosaicity and chemically etched at LETI (CEN, Grenoble, France). When the analyser and the scintillator are in vacuum, parasitic scattering as well as incoming-beam absorption are removed.

The performance of the empty (without sample) camera obtained in our laboratory is plotted in Fig. 2(a). The measurement of the scattering from a sample located at the second axis can be obtained by scanning either the vertical rotation axis of the analyser or the whole 2\( \theta \) movement, which is moved by a tangential arm with a linear encoder located at 600 mm from the sample axis. The first method is often used in European laboratories, while the second has only been used by Safinya and co-workers (Roux & Safinya, 1988). As can be seen in Fig. 2(a), with this triple-axis design and with the triple-reflection Ge crystals we used, the two methods gave equivalent results. The method of rotating the second crystal around the \( a \) axis is safer because the same spot of the monochromator surface is used, avoiding errors due to surface inhomogeneity (Deutsch, personal communication). The rocking curves obtained by these methods are compared with the theoretical triple-reflection profile: the Ge material used in our crystal should have about 10 μrad (2") mosaicity, which explains the difference in width. However, a rejection ratio of \( R = 10^{-5} \) is obtained for 1 mrad in 2\( \theta \) and a rejection factor of \( R = 10^{-4} \) is obtained for 0.1 mrad in 2\( \theta \). This can be compared to the performance of our GDPA 30 camera (made by Compagnie Générale Radiologique at Issy-les-Moulineaux, France, in 1970), where the minimum angle where useful data are recorded is limited by the beamstop size in front of the detector plane (see Table 1). The beamstop size is given by the tail of the direct beam, i.e. the beamstop extends to an angle 2\( \theta \) where the parasitic scattering is of the order of magnitude of the scattering coming from the sample. With focusing devices, this means that the beamstop size is usually ten times larger than the geometrical size of the source image (Aldissi, Henderson, White & Zemb, 1988).

In order to show the performance in units of particle size, we have plotted the same results on a logarithmic scale for \( D^* = \frac{2\pi}{q} \). Samples giving scattering below the curve cannot be precisely measured because the background exceeds the signal (Fig. 2b). A triple-reflection Ge crystal allows good rejection factors up to \( D^* \) a few hundred nanometres, while...
Table 1. Comparison of characteristics of four SAXS cameras

<table>
<thead>
<tr>
<th></th>
<th>Bonse–Hart at Saclay (France)</th>
<th>CGR camera at Saclay (France)</th>
<th>D22 at LURE, Orsay (France)</th>
<th>Huxley–Holmes camera at ANU, Canberra (Australia)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source power (kW)</td>
<td>18</td>
<td>0.8</td>
<td>DCI storage ring 1.2</td>
<td>Bent Ge 111, 6° cut</td>
</tr>
<tr>
<td>Total source size (mm x mm)</td>
<td>1 x 10</td>
<td>0.1 x 10</td>
<td>0.1 x 1</td>
<td>2-reflection Si 311</td>
</tr>
<tr>
<td>Relative brilliance (kW mm⁻²)</td>
<td>1-8</td>
<td>0.8</td>
<td>0.8</td>
<td>Bent quartz + mirror</td>
</tr>
<tr>
<td>Monochromator</td>
<td>3-reflection Ge 111</td>
<td>1 bent Ge 111, 6° cut</td>
<td>2-reflection Si 311</td>
<td></td>
</tr>
<tr>
<td>Minimum angle at which useful data are recorded (2θ, mrad)</td>
<td>0.25</td>
<td>3</td>
<td>0.3</td>
<td>5 x 10⁶</td>
</tr>
<tr>
<td>Source to monochromator (m)</td>
<td>1</td>
<td>0.3</td>
<td>0.3</td>
<td>5 x 10⁶</td>
</tr>
<tr>
<td>Sample to detector (cm)</td>
<td>60</td>
<td>48</td>
<td>150</td>
<td>0.5 x 0.3</td>
</tr>
<tr>
<td>Monochromator acceptance (μrad)</td>
<td>80</td>
<td>160</td>
<td>20</td>
<td>0.5 x 0.3</td>
</tr>
<tr>
<td>Area of entrance slit (mm x mm)</td>
<td>2 x 3</td>
<td>2 x 0.5</td>
<td>0.2 x 0.2</td>
<td>1 x 0.6</td>
</tr>
<tr>
<td>Integrated flux incident at specimen (photons s⁻¹)</td>
<td>10⁶</td>
<td>10⁶</td>
<td>10⁷</td>
<td>5 x 10⁶</td>
</tr>
<tr>
<td>Area of beam at the sample (mm x mm)</td>
<td>2 x 3</td>
<td>2 x 0.2</td>
<td>0.2 x 2</td>
<td>0.5 x 0.3</td>
</tr>
<tr>
<td>Background photons (s⁻¹/channel)</td>
<td>0.3</td>
<td>0.02</td>
<td>0.1</td>
<td>0.02</td>
</tr>
<tr>
<td>Flux at beamstop edge (s⁻¹/μrad)</td>
<td>250</td>
<td>3</td>
<td>1.6</td>
<td>3</td>
</tr>
<tr>
<td>2θ interval per point (mrad)</td>
<td>0.08</td>
<td>0.3</td>
<td>0.6</td>
<td>1.5</td>
</tr>
<tr>
<td>Beam cross section at detector (mm x mm)</td>
<td>2 x 3</td>
<td>0.2 x 8</td>
<td>0.2 x 2</td>
<td>0.2 x 2</td>
</tr>
<tr>
<td>Size of beamstop (mm)</td>
<td>–</td>
<td>3 x 8</td>
<td>2 x 2</td>
<td>2 x 10</td>
</tr>
<tr>
<td>Resolution, real space (Å)</td>
<td>6000</td>
<td>450</td>
<td>1200</td>
<td>600</td>
</tr>
<tr>
<td>Collimation ratio dv/dh</td>
<td>40</td>
<td>10</td>
<td>1</td>
<td>5</td>
</tr>
</tbody>
</table>

single-reflection Ge crystals are no better than a conventional focusing camera.

On the other hand, using only two reflections instead of six increases the available flux through the sample by a factor of four and there is the possibility of increasing the resolution by using thin slits. But in this case the resolution is limited by slits, not by Bragg-reflection divergence, and the parasitic scattering introduced by the slits is very difficult to minimize. We have chosen to work in a resolution mode where we are limited by crystals and not by slits. The only advantage of using single-reflection Ge crystals is that using a large conventional goniometer is then sufficient to obtain the required stability of the crystal axis, which is then 25 μ rad instead of 5 μ rad.

The scintillator is also placed in vacuum rotating in a horizontal plane 2α behind the analyser. An adjustable slit is placed in front of the scintillator in order to reduce the sensitive area to the exact size of the incoming beam. A pair of crossed antiscatter slits is located in front of the sample.

5. Performance

We now show the first results obtained with this arrangement, which allows high-resolution studies at low angle as well as the fine scan of one peak. We checked the relative movements and the alignment settings by using a powder of mercury behenate [CH₃(CH₂)₂COOHg], which is a surfactant with strong peaks and a large lattice (60 Å). The first four reflection orders of this rapid scan are shown in Fig. 3.

Fig. 4 shows interaction peaks in a thin dry film of monodisperse silica spheres of two different diameters. The interparticle interference behaviour is the origin of these strong peaks seen on a logarithmic scale and reflects a local packing analogous to a glass. The shape of these fine peaks and the high ratio between the direct beam and the measured small-angle scattering ensure that no significant multiple scattering occurs.

Fig. 5 shows the small-angle scattering of a dry film of latex spheres. The size of the particles is known and is consistent with the minima of the scattering function. This experiment is analogous to the one described by Bonse & Hart (1965). The intensity plotted is that after subtraction of the background (rocking curve of the empty camera).
strong increase noted at low angles is due to aggregation in large clusters during the drying process.

We turn now to liquid isotropic samples: Fig. 6(a) shows typical reverse micelles (AOT–water–oil)* at about 40 water molecules per surfactant and 0.1 M AOT (3% weight) gelified by adding cytochrome c (about 1 protein micelle). In the low-\(q\) region, the scattering is constant which is due to the distribution of protein molecules. SANS of the same sample does not show the same behaviour: the scattering is a broad peak originating from the \(\text{D}_2\text{O}\) water droplets (size 100 Å), while SAXS reflects the high electron-density (protein molecules) distribution.

The lamellar phase made with 6% didodecyl-dimethylammonium bromide (DDAB) in water spontaneously emulsifies oil in the form of polydisperse colloidal oil droplets (\(d < 1 \mu\text{m}\)) at high temperature (353 K). Between the oil droplets, the lamellar liquid crystal (observed by SANS) of periodicity 400 Å inhibits the coalescence of oil droplets. Total oil–water interface as well as the polydispersity of the oil droplets are at the origin of the scattering shown in Fig. 6(b).

Finally, we compare a sample of rat tail collagen: a bundle of wet fresh fibres (absorption at Cu \(K\alpha\) wavelength is 30%) was measured successively at station D22 at DCI, LURE, using two Si (311) parallel flat crystals as monochromators, and in our triple-axis Bonse–Hart camera. The first-order reflection is broadened owing to the resolution width of the D22 station (FWHM = \(1.5 \times 10^{-3}\) Å\(^{-1}\)) while the FWHM using the triple-reflection Ge 111 is \(3.4 \times 10^{-4}\) Å\(^{-1}\). The FWHM of the rat tail first-order reflection measured was slightly broader, \(4 \times 10^{-4}\) Å\(^{-1}\). The total collection time was 1 h at the DCI storage ring using a double symmetric Ge 111 monochromator and 20 h using the 15 kW source.

* AOT = aerosol OT = sodium 1,4-bis(2-ethylhexyl) sulfosuccinate.
6. Concluding remarks

In practical situations, the choice between the four settings compared in Table 1 is dictated by the $q$ range and the intensity $I(q)$. The crucial point is the comparison between the flux at the edge of the beamstop (or for a given rotation $2\theta$ of the analyser) and the intensity coming from the sample. Therefore, Table 1 and Fig. 2(b) are a good guide for this choice (compare with the data in Aldissi et al., 1988).

While it seems obvious that a high-resolution Bonse–Hart camera is not the optimum choice for broad peaks at $q$ values larger than $0.01 \text{ Å}^{-1}$, it is very useful to have this camera in conjunction with a classical Huxley–Holmes or conventional slit-type camera with a bent crystal, well designed for $q$ ranges between 0.01 and 0.5 Å$^{-1}$; using both diffractometers for the same samples gives a bandwidth of 3 decades in $q$ between $q_{\text{min}} = 5 \times 10^{-4} \text{ Å}^{-1}$ for the most brilliant samples and $q_{\text{max}} = 0.5 \text{ Å}^{-1}$.

The other problem with this design is that the collimation ratio of the incident beam at the sample is 40, while the collimation ratio after the sample varies between 40 and 400, depending on the vertical aperture of the slits in front of the analyser crystal. The peaks coming from the colloidal particles are observed on the raw data files and are, however, less smeared than in infinite-slit geometry; however, a reliable slit deconvolution routine such as the one developed by Strobl (1970) is still needed to measure the beam profile.

This correction step can be avoided, and this would be a major improvement, if the incoming beam at the sample position is also parallel in the sagittal direction. This is a pinhole-geometry Bonse–Hart system, using perpendicular channel-cut crystals to condition the beam before the sample. A source having enough brilliance to allow of the order of $10^9$ photons s$^{-1}$ through the sample will be available at the European Synchrotron Radiation Facility (ESRF) under construction in Grenoble, France, and this is the reason we proposed such a device should be installed at the ESRF (Zemb et al., 1990). As an intermediate step, wigglers or undulator devices at other storage rings like DORIS, SPEAR or DCI could be used to install a pinhole Bonse–Hart camera which is needed to allow routine SAXS observation of large-periodicity colloidal samples.

The design of the mechanical set-up was heavily dependent on the microdisplacement expertise of Alain Jarrossay, Head of the Bureau d’Etudes at the Microcontrôle Company (Evry, France). We thank Roland Bernon for the design and construction of high-count-rate detectors. We thank the group Matériaux pour l’Optique at LETI, Grenoble, now led by Dr Piaguet for interactive design, cutting and etching of the Ge channel-cut crystals used here. Andreas Freund, Christian Riekel and Didier Roux have given us valuable advice. We thank Steven Wilkins and his team for helping us in testing the monochromators and calculating the theoretical curve in Fig. 2(a) and Pierre Lesieur for development of the acquisition software used. Professor Strobl made his deconvolution routine available to us. We acknowledge useful advice about collimation problems from Dr D. Schwahn and an unknown referee.

References