Microbeam small-angle scattering experiments and their combination with microdiffraction

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The brilliance of undulator X-ray sources can be used to develop microfocusing optics for wide-angle (WAXS) and small-angle (SAXS) X-ray scattering. At the ESRF microfocus beamline, a beam size of 10 μm is obtained by a pinhole collimating system coupled to a double focusing mirror. This allows resolving the first order of collagen (67 nm). Glass capillary optics provides a beam size close to one micron, however, with a more limited resolution. A high resolution CCD detector allows combined SAXS/WAXS experiments for one detector setting.

1. Introduction

Laboratory micro X-ray diffraction (μXRD) techniques have been demonstrated for beam sizes at the sample position of about >10 μm for wide-angle scattering (WAXS) e.g.(Fujiwara 1960) and ≥40 μm for small-angle scattering (SAXS) e.g.(Franks 1953; Franks 1958). Measuring times for polymers or biopolymers can, however, become several hours per pattern. Micron-sized, intense X-ray beams have been obtained at 3rd generation synchrotron radiation (SR) sources (Riekel, Cedola, Heidelbach & Wagner 1997). This allows performing fast μXRD in transmission geometry on polymeric samples with a thickness above several μm (Riekel, Cedola, Heidelbach & Wagner 1997). In contrast, transmission electron diffraction (TED) is usually done for thin slices of <0.1 μm, which limits in-situ applications. The aim of the present paper is to report instrumental developments in μXRD techniques and in particular in μSAXS at the ESRF microfocus beamline.

2. Optics

X-ray microbeams down to sub-μm size at SR-sources have been generated by optical systems based on total reflection e.g.(Bilderback, Hoffman & Thiel, 1994; Iida &.Hirano, 1996 Cedola, Lagomarsino, Di Fonzo, Jark, Riekel & Deschamps, 1998), diffraction e.g.(Lienert, Schulze, Honkimaeki, Tschentscher, Garbe, Hignette, Horsewell, Lingham, Poulsen, Thomsen & Ziegler, 1998) and refraction (Snigirev, Kohn, Snigireva & Lengeler, 1996) principles. A beam of 50 nm has been obtained by glass capillary optics (Bilderback, Hoffman & Thiel, 1994). For μ-SAXS at an undulator source, larger beam sizes are usually necessary in view of requirements of flux density and beam divergence (Riekel, Engström & Martin, 1998). Bragg-Fresnel (BF) optics have been used to demonstrate small-angle scattering (SAXS) with a 3 μm^2 spot (Snigirev, Snigireva, Riekel, Miller, Wess & Wess, 1994). Circular BF-lenses can, however, only be used in near back reflection geometry, which reduces the band pass by about factor 100. This results in a generally too low flux density for experiments on thin polymer and biopolymer samples.

The microfocus beamline (Fig.1) uses a Si-111 double monochromator combined with an ellipsoidal mirror (Engström, Fiedler & Riekel, 1995). The focal spot of 20(h)*40(v) μm^2 is blurred by mirror imperfections. A beam definition device such as a collimator or glass capillary is therefore placed in the focal plane.

3. Resolution

Fig.2 shows a micro-collimating system based on electron microscopy Pt-apertures. A good order resolution and the capability to reach small s-values ($s=1/d=2\sin\Theta\,\lambda^{-1}$) are required for SAXS experiments. The order resolution –Δs- can be defined as:

$$\Delta s=((\Delta\alpha/\lambda)^2+(\Delta\alpha_d/\lambda)^2)^{0.5} \text{ with } \Delta\alpha_d=((b^2+PSF^2)/L_D)^{0.5} \qquad (1)$$

$\Delta\alpha$ is the beam divergence at the sample position, $\Delta\alpha_d$ is the angular acceptance of the detector, b the size of the beam on the detector and PSF the point-spread-function of the detector (Riekel, Bösecke, Diat & Engström, 1996). The variation of Δs for a vertical beam divergence of 0.2 mrad (Fig.1) and a 10 μm beam is shown in Fig.3.a. By using a CCD camera with a PSF of ≈0.1 mm the order resolution can be optimized for $L_D \leq 600$ mm which is also of interest for experiments on protein microcrystals (Cusack, Belrhali, Bram, Burghammer, Perrakis & Riekel 1998).

The minimum scattering vector attainable –s_{min}- can be derived from: (Chu, Harney, Li, Linliu & Yeh, 1994)

$$s_{min}=\sin[(A_d+A_g)/2L_2 + A_g/2L_D+PSF/2L_D]\lambda^{-1} \qquad (2)$$

where A_d, A_g, L_D are defined in Fig.2. Fig.3.b shows the variation of the maximum d-value ($1/s_{min}$) for typical values of λ=0.096 nm, A_d=10 μm and A_g=20 μm. Calculated d_{max}-values are similar to those of a SAXS camera at 2nd generation bending magnet SR-source with a beam sizes of 1 mm^2 (Elsner, Riekel & Zachmann, 1985). This reflects the difference in source brilliance. Fig.4 shows that the first order of a rat's tail collagen fiber (67 nm) can just be resolved.

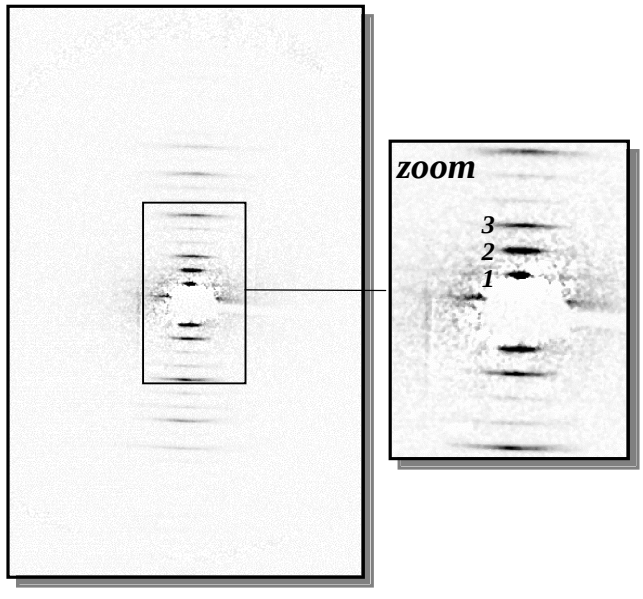

Figure 4
SAXS pattern of a rats tail collagen fiber.(λ=0.078 nm; 10 μm beam; *MAR*-CCD detector with 16 bit readout). Beamstop displaced to observe first order (d=67 nm).

In routine operation one obtains rather $s_{min} \approx 2*10^{-2}$ nm^{-1}. A further reduction of the defining aperture to 5 μm without sacrificing too much flux is feasible. Glass capillary optics has allowed reaching a

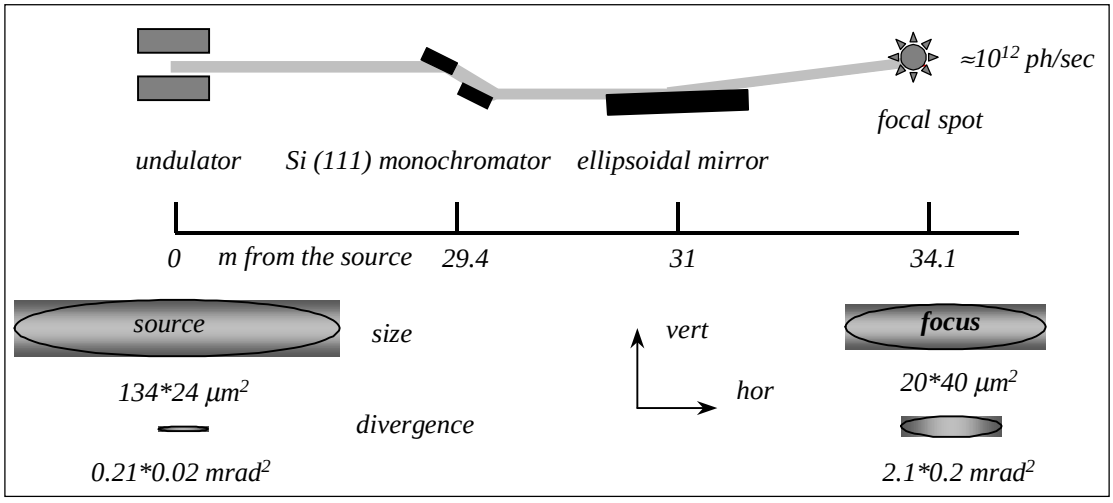

Figure 1
Schematic design of optical system of the ESRF microfocus beamline. The figure also shows the size and divergence of the beam at the low-β undulator source point and at the focal spot.

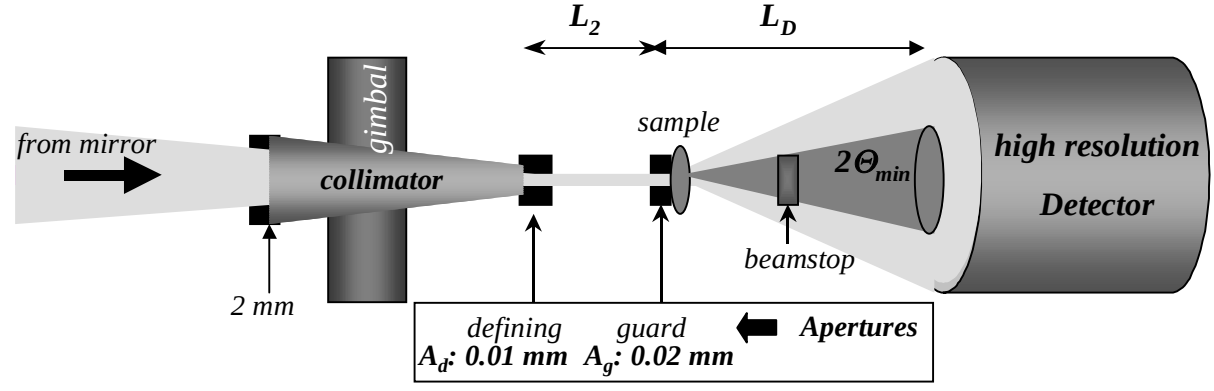

Figure 2
Schematic picture of pin-hole collimating system based on electron microscopy Pt-apertures. The beam from an ellipsoidal mirror is focused onto the defining aperture.

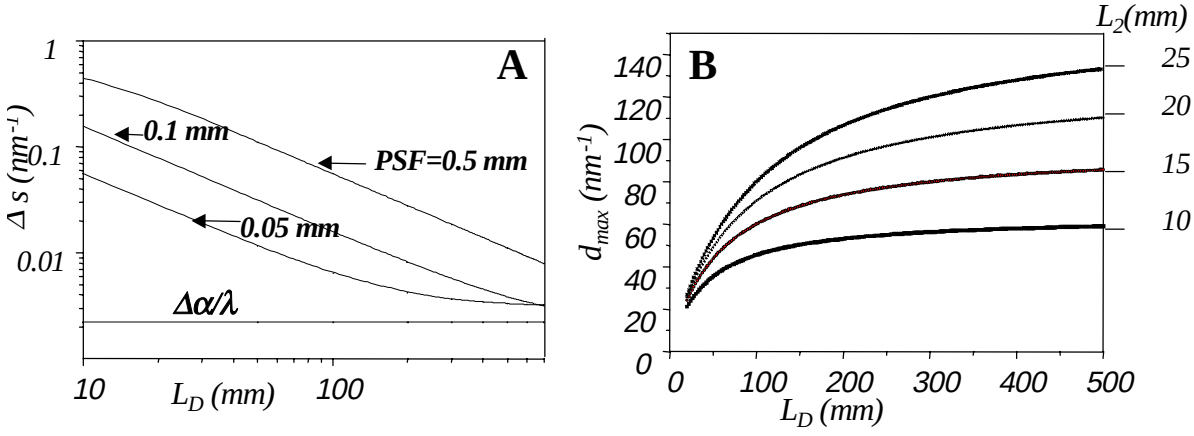

Figure 3
A. Variation of order resolution –Δs- as a function of detector-to-sample distance –L_D- for different point-spread-function (PSF) values
B. Variation of maximum d-value –d_{max}- attainable. λ=0.096 nm; see Fig. 2.

beam size of ≈3 μm but for a lower resolution of s_{min}≈7*10^{-2} nm^{-1} (Engström & Riekel 1996). This is due to the fact that the guard aperture has to block diffuse scattering directly at the exit of the capillary.

As a consequence of the compact SAXS-optics it becomes feasible to perform combined SAXS/WAXS experiments for a single detector setting while maintaining a value of s_{min}≈2*10^{-2} nm^{-1} (Fig.3.b). Fig.5 shows the variation of the scattering pattern of a stretched polyethyleneterephthalate (PET) foil as a function of the distance sample to detector. The 300 μm diameter beamstop cuts the scattering pattern at s_{min}≈0.05 nm^{-1}. s_{min} could be further reduced by increasing the distance beamstop-to-sample or reducing the beamstop diameter (Fig.3.b). An as small as possible beamstop is, however, preferable in order to reduce air scattering background. This technique could be of interest for in-situ polymer extrusion experiments e.g.(Cakmak, Teitge, Zachmann & White 1993).

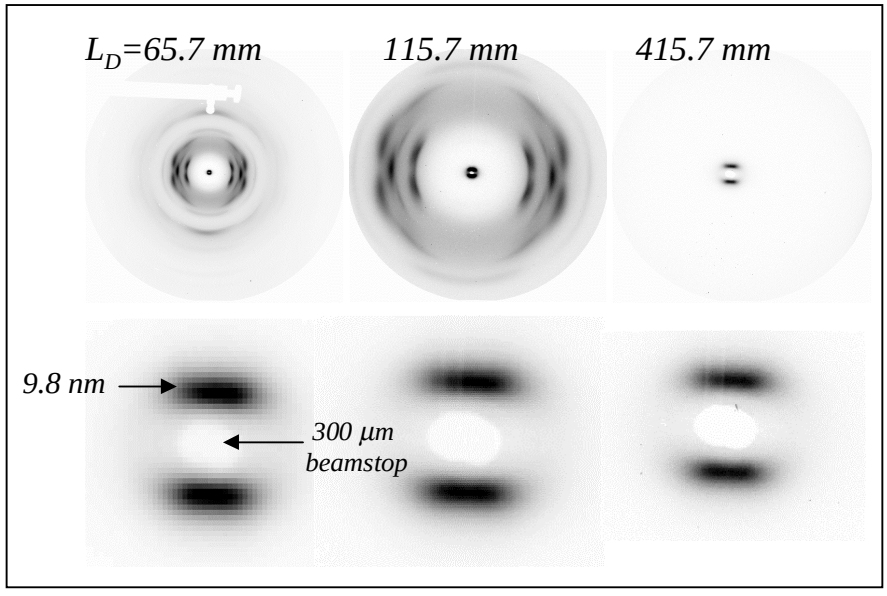

Figure 5
Diffraction pattern of stretched PET foil for several sample-to-detector distances. The lower part of the patterns shows the central SAX-range. The long period of ≈9.8 nm can be observed already at L_D=65.7 mm. Edge of detector for L_D=115.7 mm corresponds to d≈0.19 nm. (λ=0.096 nm; 10 μm beam; *MAR*-CCD detector:ϕ=130 mm, PSF=0.1mm)

4. Practical use

The reduction of beam size to ≤10μm (see above) necessitates a high-resolution microscope at the instrument and automatic sample alignment techniques. A detector with high detector quantum efficiency (DQE) is required in order to limit beam damage of organic matter as far as possible. At the present stage a *MAR*-CCD (16 bit readout; cooled to -100^0C) with 130 mm entrance window and about 4 sec readout (webpage: www.mar-usa.com) is used for the highest requirements in DQE. A 10 Hz/12 bit readout *Photonics Science XIDIS*-detector (Peltier cooled; webpage: www.photonic-science.ltd.uk) is used for scanning applications. The camera described above has amongst others allowed to determine the fibril orientation in flax fibers (Müller, Czihak, Vogl, Fratzl, Schober & Riekel, 1998) and the lamellar morphology in starch grains (Waigh, Perry, Riekel, Gidley & Donald, 1998) from the low-angle scattering region.

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