

# Three-dimensional imaging of paper by use of synchrotron x-ray microtomography

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## ABSTRACT

In order to be able to describe and understand the mechanical properties of paper it is essential to know its three-dimensional structure on a micrometer scale; yet reliable, non-destructive and non-disturbing imaging methods are scarce. In the present work it is demonstrated that x-rays from a *third generation* synchrotron beam line, which is characterised by a high brilliance, a high degree of uni-directionality and of a considerable degree of transvers spatial coherence, constitute an ideal tool for micro-tomographic imaging, based on using phase contrast.

## INTRODUCTION

Paper is a porous material where the pore structure in most paper grades is a continuous three-dimensional network of voids. In the same manner the solid material, fibres and fillers, also forms a continuous three-dimensional network. From measurements where the pore structure is characterised by the density of the paper, we know that important paper quality parameters like opacity, liquid sorption and printability strongly depend on the pore structure. It is thus important to be able to measure or calculate the porous structure of paper. This has been done by very different approaches. Various porosimetry methods, light-, electron- and confocal-microscopy and mathematical modelling have been applied as tools to assess the three-dimensional structure of paper.

Mercury and liquid porosimetry methods yield a pore size distribution, but no information of where the pores are and how they are connected. The results will not only depend on the pore size distribution of paper but also on the dimensions of the more narrow necks connecting larger pores [1].

A more direct approach is to measure e.g. the filler distribution [2] or density distribution [3] of cross sections of paper from images of paper cross sections obtained in a light or electron microscope. This yields information on how the mass in the paper is distributed in two dimensions. If several such two-dimensional successive images are combined in a 3D-volume rendering image analysis programme a good representation of the 3D-structure of the paper may be obtained [4]. This is however very work intensive and only small 0.2 mm x 0.2 mm paper areas have been studied.

The confocal laser scanning microscope (CLSM) has been applied to measure the three dimensional surface pore structure of paper [5], [6]. It is however not possible to measure the interior layers of the paper because the light beam is refracted by the outer fibre layers and thus the focus and signal strength soon falls beneath the detectable range.

Different pore volume models have been proposed. Niskanen [7] has developed a programme (KCL-PAKKA) which models the paper structure by dropping single fibres with defined length and bending stiffness distributions until a sheet of wanted basis weight is formed. The pore structure of the sheet is then easily found. Dodson [8] has deduced the pore size distribution of a two-dimensional (MD-CD) sheet as a function of basis weight. This approach only yields realistic values for very thin sheets. Kettle [1] evaluated three pore models for SC-paper. As input parameter he used the pore volume distribution as measured by Mercury and liquid porosimetry. The absorption rate of water was calculated from the models and compared to experimental results.

None of the methods reviewed yields a 3D-representation of paper in a non-destructive manner, thus there still is need for a non-destructive 3D-imaging system for paper. The present work is concerned with the use of synchrotron x-ray microtomography for that purpose.

## MICROTOMOGRAPHY

*Tomography* is a method for three-dimensional imaging frequently used in materials technology and in medicine. For length scales larger than a few centimeters it is known as *Computer Tomography* (CT), in particular in connection with the use of x-ray beams, or *NMR-imaging* when microwaves in the nuclear magnetic resonance regime are used. The method consists of taking a large set of images ( $N$ ) of the beam transmitted through the sample while the sample is rotated to different positions (rotation angle  $\theta$ ) for each image taken. Each image  $p(u, v, \theta)$  (on coordinate system of the two-dimensional detector,  $(u, v)$ ) is then a projected picture of the *stopping power distribution*  $\rho(x, y, z)$  within the sample (as described by the sample-fixed coordinate system  $x, y, z$ ).

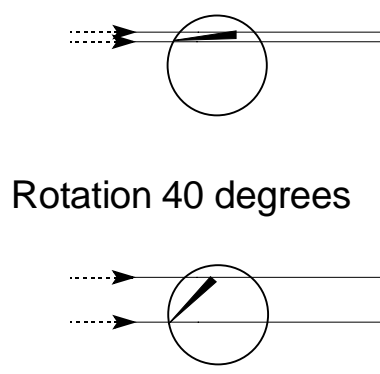


Fig.1 Tomography: Illustration of the X-ray beam sensing of an inhomogeneity in a cylindrical object at two angular positions  $40^\circ$  apart, as projected on to a detector screen.

From the set of projected images  $p(u, v, \theta)$  the interior of the sample material can be reconstructed in terms of the function  $\rho(x, y, z)$ . The accuracy of the reconstruction depends upon the quality of the observed  $p(u, v, \theta)$ 's and on the number of images  $N$ . Mathematically the reconstruction is known as a *Radon* transformation, which is of the form of a *Fourier*-like integral having to be approximated by the finite sum of the  $N$  observed  $p(u, v, \theta)$ 's [9].

The reconstruction transformation is now-a-days a routine operation with any tomography installation.

*Micro-tomography* is the notation applied when the sample dimensions are below centimeter range, but the principles are otherwise identical with those just described.

Microtomography with x-rays requires an x-ray beam with high degree of beam parallelism, preferentially with high brilliance and with good penetration ability. For these reasons x-rays of high photon energies from synchrotron sources are needed.

It is noteworthy that tomography is performed directly on the sample material without the need to introduce contrast material or epoxy binder, as is required for some alternative imaging methods like *SEM*. Furthermore, the three-dimensional imaging is achieved without slicing the material. The method is both non-invasive and non-destructive. By application of appropriate imaging handling software, cross-sectional pictures in arbitrary directions can easily be obtained from the tomographic data set.

## PHASE CONTRAST

The most obvious way of providing the necessary contrast for imaging is by using beam *absorption*. Since heavy elements absorb x-rays more than light elements, Wilhelm Conrad Röntgen was able from the very moment of the discovery of x-rays to image the bones (with calcium) of the body through the less dense tissue (with mostly hydrogen, carbon, nitrogen and oxygen), and the absorptive imaging method with x-rays remains the most important and most used. However, absorptive contrast is not available in order to see the internal structure in materials like celluloses and other organic polymers because they normally contain only the light elements mentioned. For such materials one may use *phase* contrast instead.

Phase contrast is well known in the optics of regular visible light [10]. The optical path length is different for a wave passing through the object material due to the finite refractive index ( $n$ ), than for a wave passing only through the surrounding medium (for instance air or water, refractive index  $n_m$ ), and the phase difference thus imposed on the two waves will make them interfere constructively and destructively to produce a set of interference fringes just behind the object. The phenomenon is closely related to what is known as *Fresnel diffraction*. The edges of the object will become visible through these fringes, which is in fact the *phase contrast*. It is noteworthy that contrasts by phase is much more sensitive than contrast by absorption. For x-rays the index of refraction is very close to unity, as found by the following formula [11]:

$$n = 1 - r_e \lambda^2 \sum_j Z_j / (2\pi V) \quad (1)$$

where  $r_e = 2.8 \cdot 10^{-15}$  m is the classical electron radius,  $\lambda$  is the wavelength,  $V$  is the volume and  $Z_j$  is the atomic mass of the  $j^{\text{th}}$  atomic species, over which the sum should be taken.

For instance one finds  $n$  to be 0.99999904 for cellulose for wavelengths 0.65 Å, yet this small deviation from unity is sufficient to see the edges of individual cellulose fibres of dry paper samples (Fig.2).

It is also noteworthy and of utmost importance that there is expected to be sufficient contrast between cellulose and water, so that also wet paper can be studied, because the calculated index of refraction for water is 0.99999937, giving a *relative* index between the two materials of 0.99999967.

However, phase contrast can only be obtained when the beam is at least partially *spatially coherent*. This is the case for x-rays obtained from *third generation* synchrotron sources with *undulator insertion devices* (See next section). The use of phase contrast for microimaging has been pioneered by Snigirev and coworkers at the European Synchrotron Radiation Facility (ESRF) [12, 13].

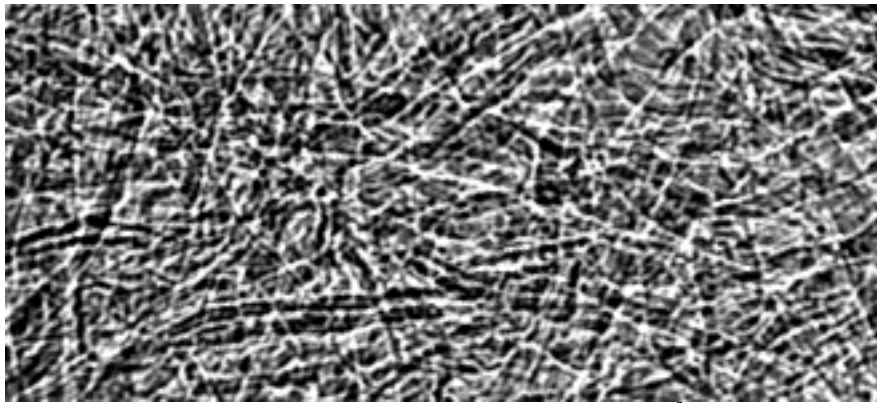


Fig.2 Part of a single exposure of dimension approximately  $200 \times 375 \mu\text{m}^2$ .

## EXPERIMENTAL

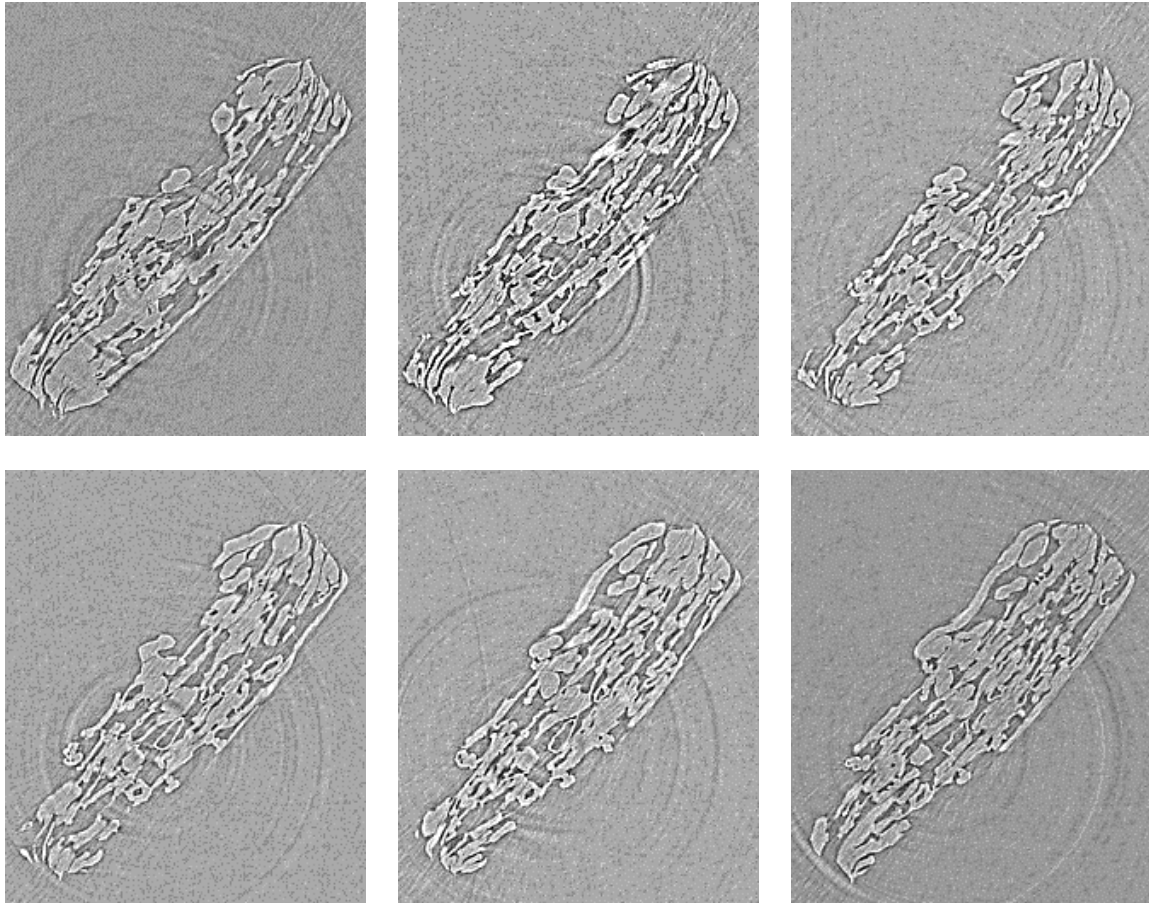
The experiments were performed at the *ID 22 MICRO-FID* beam-line (BL 24) at the European Synchrotron Radiation Facility (ESRF) in Grenoble [14]. The beam-line is specially designed for micro-fluorescence ( $F$ ), micro-imaging ( $I$ ) and micro-diffraction ( $D$ ), using an undulator beam of small source dimension. A photon energy of 19.2 keV (0.65 Å wavelength) was extracted from the beam by means of a Si [111] monochromator. The transmitted beam is recorded by an ultra high resolution (0.8 μm) Charge Coupled Device (CCD)-camera, specially developed at the ESRF [15].

The paper sample studied is a hand sheet of soft wood kraft pulp. A strip about 10 mm long and 0.5 mm wide of thickness 0.5 mm was gently cleaved to a thickness of about 0.1 mm and mounted horizontally in the rotatable sample holder. There were taken 1280 exposures (at every 0.28 degree of rotation), with exposure time 5 seconds each. An example of a single exposure is shown in Fig.2.

## RESULTS

As an example of the results that can be obtained we show in Fig.3 six reconstructed cross sections of the paper strip, at intervals of  $4.8\ \mu\text{m}$ . Also narrower intervals can be chosen for the presentation (multiples of  $1.2\ \mu\text{m}$  in the present case).

An indication of the type of limitations of the method can be seen by the artefact in the form of ring-shaped “shadows”, which derive from the reconstruction procedure involving a finite number of exposures. However, a lot of details of the internal structure can be discerned, both in each individual cross section and from picture to picture:



*Fig.3 A sequence (left-to-right upper, then left-to-right lower) of reconstructed cross sections at interval  $2.4\ \mu\text{m}$  along the strip. Each frame is of dimension  $240\ \mu \times 300\ \mu\text{m}$ , the section dimension being about  $85\ \mu\text{m} \times 300\ \mu\text{m}$*

Cross sections of individual fibres, of typical size  $15 \times 30$  micrometers, can be discerned. Most fibres appear as massive, however this may not be only due to collapse, as the thickness of a single fibre wall is close to the resolution limitation of the method. For four to five cases the resolution is sufficient to see the walls of the fibre tubes.

Very many individual fibres can be identified to extend through all the sections. They are of course fibres that are oriented more or less parallel to the paper strip. Inclined fibres appear as thread-like features on each section (f. i. upper side of section 2 and 3).

As individual fibres can be identified from section to section, a full three-dimensional analysis can be performed. A detailed study over several sections (not shown), show that well-defined fibre tubes sometimes develop into a damaged and fibrillated shape close to the end.

By studying series of images it is confirmed that hand sheets are highly layered structure. The fibres are not woven into each other in the z-direction. By following individual features over extended ranges (more than 50 microns) along the strip practically no cases of fibre interconnections between the layers can be found.

A lot of voids is seen to exist between the fibres, amounting to 30 – 40 % of the section areas. The voids are mutually connected, with narrow passages between wider channels. Unlike the fibres, the voids are connected three-dimensionally (not necessarily apparent from Fig.4), illustrating filtering ability of the paper.

Paper deformation at the edges can be seen, caused by cutting by knife.

## DISCUSSION

*Paper* is an example of a *porous* material, a category of materials that is attracting considerable attention both from a practical as well as from a conceptual point of view [5]. From Fig.4 it is evident that microtomography offers a way to obtain a very detailed statistical description of the paper material on a micrometer scale. The *density* and the degree of *porosity* are readily obtainable, as well as distribution functions of channel dimensions. One may furthermore establish directional-dependent correlation functions of the local density  $\rho(r)$ :

$$C(r) = \int_V \rho(r') \rho(r + r') dr' \quad (2)$$

where the integral runs over the sample volume  $V$ . Average effective fibre dimensions should be obtainable from this function, and the anisotropy of its central peak could be taken as a measure of the sample anisotropy. One should also be able to establish a measure of channel connectivity (“percolation”) to characterise the fluid penetrability of the material.

Also statistics on single fibres might be obtained, although other methods for settling such statistics may be easier: Fibre length distributions, fibre collapse distributions, fibre direction distributions, fibre bending or buckling distributions.

We intend to return to such analyses.

The present study of *dry* material could in a future development be extended to studies of *wet* paper. A unique feature of microtomography is that studies of wet paper should be feasible. One has to ensure, of course, that the wet paper does not deform during the rotating operation in the beam, either by rotating around a *vertical* axis, or by keeping it in a thin-walled glass capillary. In the latter case it could be even totally *soaked*.

Wetting with water is expected to not only fill the pores, but also to give rise to substantial swelling of chemical fibres and *de-collapse* of mechanical pulp fibres in calandered sheets. One may even want to investigate to what extent the de-collapsed state will survive a re-drying process.

Also the effect of printing agents, or of the application of organic solvents, less apt to wet the fibres than water, might be interesting to study, like octane or decane. The partial replacement of such liquids by water could be another interesting feature.

## CONCLUSIONS

In this preliminary study we demonstrate how x-ray microtomography using coherent beams from a third generation undulator synchrotron source can be applied for non-destructive, non-invasive three-dimensional imaging of paper on a micrometer scale.

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